

I. The Volumetric Determination of Vanadium and Chromium in Special Alloy Steels. II. Ceric Sulfate as a Volumetric Oxidizing Agent

---

A DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS  
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY  
IN THE UNIVERSITY OF MICHIGAN

---

By  
Philena Young

1928

---

EASTON, PA.:  
MACK PRINTING COMPANY  
1928





I. The Volumetric Determination of Vanadium and Chromium in Special Alloy Steels. II. Ceric Sulfate as a Volumetric Oxidizing Agent

---

A DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS  
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY  
IN THE UNIVERSITY OF MICHIGAN

---

By  
Phílana Young

1928

---

EASTON, PA.:  
MACK PRINTING COMPANY  
1928





## CONTENTS

### PART I

#### The Volumetric Determination of Vanadium and Chromium in Special Alloy Steels

|                                                                                                                | Page |
|----------------------------------------------------------------------------------------------------------------|------|
| I. Vanadium in Chrome-Vanadium-Tungsten Steels.....                                                            | 7    |
| II. Persulfate Method for Chromium Plus Vanadium in Chrome-Vanadium-Tungsten Steels (Modified Procedures)..... | 19   |

### PART II

#### Ceric Sulfate as a Volumetric Oxidizing Agent

|                                                                                          |    |
|------------------------------------------------------------------------------------------|----|
| I. The Preparation and Standardization of Solutions. The Determination of Calcium.....   | 24 |
| II. The Determination of Iron.....                                                       | 36 |
| III. The Titration of Iodide.....                                                        | 41 |
| IV. The Determination of Arsenic.....                                                    | 46 |
| V. The Determination of Antimony.....                                                    | 50 |
| VI. The Volumetric Determination of Cerium.....                                          | 53 |
| VII. The Determination of Vanadium in the Presence of Chromium, Tungsten and Iron.....   | 60 |
| VIII. The Determination of Chromium in the Presence of Manganese, Iron and Vanadium..... | 67 |
| IX. The Preparation and Stability of Solutions.....                                      | 78 |



Digitized by the Internet Archive  
in 2026

### ACKNOWLEDGMENT

It is a pleasure to acknowledge my indebtedness to Professor H. H. Willard for the suggestion of this investigation and to express my appreciation of his advice and interest throughout the work.

PHILENA YOUNG

## PART I

### The Volumetric Determination of Vanadium and Chromium in Special Alloy Steels

- I. Vanadium in Chrome-Vanadium-Tungsten Steels
- II. Persulfate Method for Chromium Plus Vanadium in Chrome-Vanadium-Tungsten Steels (Modified Procedures)



# Vanadium in Chrome-Vanadium-Tungsten Steels

## Volumetric Determination

THE most rapid and satisfactory methods for determining vanadium in alloy steels are those which involve no separation of this metal from chromium and iron, but depend on differential oxidation or reduction. The present methods based upon this principle are:

(1) Permanganate titration<sup>1</sup> of a vanadyl salt obtained by reduction (a) with hydrochloric acid,<sup>2</sup> a long and tedious process; or (b) with ferrous sulfate, the excess being removed by ammonium persulfate,<sup>3</sup> a method in which the accurate determination of the end point is difficult due to the color, especially if there is a large quantity of chromic salt in the solution. This titration has been made electrometrically,<sup>4</sup> but such a method is not recommended unless conditions can be found to improve greatly the break at the end point.

(2) Oxidation with boiling nitric acid<sup>5</sup> to vanadic acid which is titrated with ferrous sulfate electrometrically, a process in which the oxidation is not quite complete.

(3) Reduction of chromic acid by hydrogen peroxide in acetic acid solution;<sup>6</sup> the vanadic acid is not affected and is titrated with ferrous sulfate. In this process the end point has been determined electrometrically and also with diphenylamine as internal indicator.<sup>7</sup>

(4) Another indicator method in the titration of vanadic acid with ferrous sulfate involves the use of potassium ferricyanide as internal indicator.<sup>8</sup> However, the large blank required for the indicator and the indistinctness of the color change at the end point are serious disadvantages.

The object of the present investigation was to obtain a new method for vanadium in alloy steels, which would be both rapid and accurate.

<sup>1</sup> Kelley and Conant, *J. IND. ENG. CHEM.*, **8**, 719 (1916).

<sup>2</sup> Campagne, *Ber.*, **36**, 3164 (1903).

<sup>3</sup> Hamner, *Met. Chem. Eng.*, **17**, 206 (1917).

<sup>4</sup> Kolthoff and Tomicek, *Rec. trav. chim.*, **43**, 447 (1924).

<sup>5</sup> Kelley, Wiley, Bohn, and Wright, *J. IND. ENG. CHEM.*, **11**, 632 (1919); **13**, 939 (1921).

<sup>6</sup> Willard and Fenwick, *J. A. C. S.*, **45**, 84 (1923).

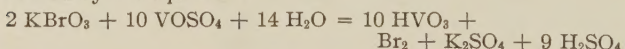
<sup>7</sup> Furman, *IND. ENG. CHEM.*, **17**, 314 (1925).

<sup>8</sup> Johnson, "Chemical Analysis of Special Steels, Steel Making Alloys and Graphites," p. 6, John Wiley and Sons, Inc., 1920.

### Preliminary Experiments

Preliminary experiments showed that chlorine oxidized vanadium quantitatively in acid solution but had a very slight effect on chromic salts. Since a method using chlorine gas as the oxidizing agent would be inconvenient, this same principle was followed further by testing the action of various oxidizing agents in a hydrochloric acid solution containing chromic and vanadyl salts. Only those were considered, the excess of which could be easily removed. Experiments were carried out with potassium chlorate, potassium bromate, precipitated manganese dioxide, potassium permanganate, sodium bismuthate, and potassium persulfate. The first two were very effective, but the excess of chlorate, unlike bromate, could not be readily removed. Precipitated manganese dioxide oxidized chromic salts almost completely even in a solution containing 15 cc. of concentrated hydrochloric acid per 100 cc., an indication that the oxidation in this case is caused, not by chlorine, but largely by the manganese dioxide. Potassium permanganate and sodium bismuthate gave quantitative results only within such a very narrow range of hydrochloric acid concentration that a method based on their use would not be practical. Persulfate did not completely oxidize vanadyl salts in hydrochloric acid solution.

Further experiments showed that bromate oxidizes vanadium quantitatively in a solution containing ammonium sulfate and a definite concentration of hydrochloric acid without oxidizing chromic salts. The reaction may be represented by the equation:



Unless both ammonium salts and hydrochloric acid are present, the excess of bromate is not destroyed by boiling.

There is at present no method for determining vanadium in the presence of chromium, iron, and tungsten. The tungsten is always removed in the form of tungstic acid, and this precipitate carries with it some chromium and vanadium as impurities. It was found in the present work that, after dissolving the tungstic acid in sodium hydroxide, this solution of sodium tungstate could be poured back into the original filtrate, to which additional iron in the form of ferric alum had been added, without any precipitation of tungstic acid, provided that the concentration of hydrochloric acid present was not too great. The exact action of the ferric salt is not clear. This avoids the error due to the presence of vanadium in tungstic acid, and the principle may be used for determining this element electrometrically in tungsten steels.

Tungstic acid makes impossible the use of an indicator and must, therefore, in this case be completely removed. The estimation of the small amount of vanadium in this precipitate offers considerable difficulty. Kelley<sup>5</sup> found that an excess of a

uranyl salt in an ammoniacal solution containing tungstate and a small amount of vanadate carried down the latter completely; the author has been unable to confirm this result; Willard and Fenwick<sup>6</sup> determined it in a phosphoric acid solution containing the tungsten as soluble phosphotungstic acid by electrometric titration with ferrous sulfate but the end point was not very satisfactory. Furman<sup>7</sup> dissolved the tungstic acid in strong ammonia and, after the addition of alum, made the solution faintly ammoniacal. The precipitate, which carried down the vanadium present, was dissolved and added to the original solution. The author could not check this method, nor were thorium or zirconium salts found more effective than alum for this purpose. Clarke<sup>9</sup> found that cupferron precipitated small amounts of vanadium from a solution containing tungstic acid, hydrofluoric acid, and some hydrochloric acid.

In the following work a colorimetric method was used. The tungstic acid with impurities was fused with sodium carbonate or dissolved in sodium hydroxide, the liquid filtered from suspended matter, and the solution acidified with phosphoric acid. The intensity of color of the yellow vanadotungstic acid is proportional to the concentration of vanadium, but practically independent of the amount of tungsten or phosphoric acid. Ferric iron in moderate amount does not interfere.

#### End Point in Vanadic Acid Titration

In the electrometric titration a platinum-0.1 *N* KCl-AgCl electrode system was used. To keep the electrodes in sensitive condition, two methods were especially satisfactory. In one the electrodes were charged with oxygen<sup>10</sup> by making them the anode in a 25 per cent perchloric acid solution; in the other they were allowed to stand in a 0.5 *N* ceric sulfate solution when not in use. The second process, being the simpler, was adopted. It was also noticed that the magnitude of the break at the end point was very largely dependent upon the temperature of the solution at the time of titration, a fact observed by Kelley and his collaborators,<sup>5,11</sup> and upon the concentration of iron. The author obtained excellent results with solutions cooled to 5-8° C., and with pretreated electrodes, even with 5 grams of iron present.

Reference has been made to the use of diphenylamine as an internal indicator in this titration.<sup>7</sup> Cone and Cady<sup>12</sup> found in the zinc titration with ferrocyanide that diphenylbenzidine gave the same color change as diphenylamine and required no blank correction. When diphenylbenzidine was used in the vanadic acid titration, an excellent end point was obtained if

<sup>9</sup> *Analyst*, **52**, 467 (1927).

<sup>10</sup> The effect of anodic and of cathodic polarization on the break at the end point with monometallic systems was studied by Willard and Fenwick, *J. A. C. S.*, **44**, 2524 (1922).

<sup>11</sup> Kelley and Conant, *Ibid.*, **38**, 341 (1916).

<sup>12</sup> *Ibid.*, **49**, 356 (1927).



phosphoric acid was present and sufficient sodium acetate to react with the strong acid in the solution. The blank correction is much smaller than that required with diphenylamine. Back titration with an oxidizing agent in this buffered solution is not possible because the purple color returns very slowly.

### Experimental

The direct oxidation of vanadyl sulfate by electrometric titration with potassium bromate proved to be much too slow, either in a cold or hot solution, to be of any practical value.

Because a method for determining vanadium in the presence of chromium is of especial value in the analysis of alloy steels, quantities of vanadium, chromium, iron, and tungsten, approximating the amounts found in steels, were used in the following work. The iron was in the form of a ferric ammonium alum solution. To this was added chromium sulfate, vanadyl sulfate which had been accurately standardized, and, after diluting somewhat, hydrochloric acid and potassium bromate. Ammonium salts were already present from the ferric alum. After the oxidation, the solution was boiled to destroy excess of bromate (8 minutes boiling was always sufficient, and 15 minutes not harmful), cooled to 5° C., and after the addition of 25 cc. ice-cold sulfuric acid, sp. gr. 1.5, titrated electrometrically with 0.025 *N* ferrous sulfate.

Preliminary experiments having shown that the oxidation of vanadium in the presence of considerable chromium and iron was selective and that the requisite amount of hydrochloric acid for a quantitative determination depended largely upon the amount of iron in the solution, the acid range permissible for samples containing 1 to 5 grams of iron was determined.

Each solution used in Table I contained 23 mg. vanadium, 100 mg. chromium, 1.5 grams potassium bromate, and the stated amounts of iron and hydrochloric acid, sp. gr. 1.18. The volume at the time of oxidation was 300 cc., and 50 cc. of sulfuric acid, sp. gr. 1.5, were added just before titration. The solution containing the bromate was allowed to stand 15 minutes on the hot plate and was then boiled 8 minutes. Later work showed that the same results could be obtained with a volume of 200 cc. at the time of oxidation and the addition of 25 cc. of sulfuric acid, sp. gr. 1.5, just before titration.

Though it may appear from this table that the acid range for any given case is narrow, an acid concentration in which the error amounts to as much as 0.25 mg. vanadium would not be very unsatisfactory if a sufficiently large sample was used—i. e., at least a 6-cc. variation in hydrochloric acid content is possible.

Further experiments in which the amount of bromate was varied from 1 to 2 grams and the chromium from 50 to 200 mg.

Table I—Effect of Concentration of Hydrochloric Acid and of Iron  
Error in mg. V for cc. of HCl, Sp. Gr. 1.18, Specified per 100 cc. of Solution Present at Time of Oxidation<sup>a</sup>

| IRON<br>Grams | 1 cc. | 2 cc. | 3 cc. | 4 cc. | 5 cc. | 6 cc. | 7 cc. | 8 cc. | 9 cc. | 10 cc. |
|---------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|
| 0             |       |       |       |       |       |       |       |       |       |        |
| 1             |       |       |       |       | +0.02 |       |       |       |       | +0.01  |
| 2             |       |       |       |       | +0.05 | +0.25 |       |       |       |        |
| 3             |       |       | +0.20 | +0.32 | 0.00  | 0.00  | +0.02 | -0.05 |       |        |
| 4             |       | +0.23 | +0.02 | +0.05 | -0.04 | -0.15 | -0.16 |       | -0.25 |        |
| 5             | +0.18 | +0.02 | -0.06 | 0.00  | -0.19 |       |       |       |       |        |

<sup>a</sup> Each error in mg. of V represents the average of a number of titrations which agreed closely.

indicated that the percentage of hydrochloric acid which must be present at the time of oxidation of the vanadium becomes progressively higher as the amount of either of these materials is increased. It was found best to use 1.5 to 2 grams of bromate. Table I can be employed as a reference table and the general rule adopted that, when the chromium content of the sample is known to be smaller than 100 mg., the lower possible concentration for hydrochloric acid indicated there be used. For a sample containing more than 100 mg. of chromium the higher concentration of acid would be better.

*Effect of Presence of Tungsten*—Attempts to titrate vanadic acid electrometrically in the presence of 100 mg. of chromium, 5 grams of iron, and 1 gram of tungsten (either in the form of phosphotungstic acid or of solid tungstic acid) were not successful, the results being very low. The presence of free phosphoric acid was not harmful if tungsten was absent.

In the experiments shown in Table II there were present the indicated quantities of iron, 100 mg. chromium, 23 mg. vanadium, and 4 cc. hydrochloric acid, sp. gr. 1.18. To this solution the stated amount of tungsten in the form of sodium tungstate was added and sufficient water to make the volume 200 cc. The vanadium was oxidized by bromate, the excess destroyed by boiling, the solution cooled to 5–8° C., and 25 cc. sulfuric acid, sp. gr. 1.5, added before titration with 0.025 *N* ferrous sulfate.

Table II—Effect of Presence of Tungstic Acid

| No. | Fe           | W           | ERROR IN<br>MG. V | No. | Fe           | W            | ERROR IN<br>MG. V |
|-----|--------------|-------------|-------------------|-----|--------------|--------------|-------------------|
|     | <i>Grams</i> | <i>Gram</i> |                   |     | <i>Grams</i> | <i>Grams</i> |                   |
| 1   | 5            | 0.02        | +0.02             | 5   | 5            | 0.80         | −0.25             |
| 2   | 5            | 0.08        | +0.06             | 6   | 5            | 1.00         | −0.22             |
| 3   | 5            | 0.12        | −0.06             | 7   | 4            | 1.00         | −0.32             |
| 4   | 5            | 0.40        | −0.06             | 8   | 2            | 1.00         | −0.76             |

In experiments 4, 5, 6, and 7 the tungstic acid precipitated out to some extent, but went into solution as the liquid was heated and remained in solution throughout the analysis. In No. 8 a considerable quantity of tungstic acid remained in the solid form throughout the analysis. These results indicate that the solubility of tungstic acid is due to the presence of ferric salts. It thus becomes possible to simplify considerably the analytical procedures in use for vanadium in alloy steels.

### Analysis of Alloy Steels—Electrometric Method

#### *Recommended Procedure*

(1) **VANADIUM IN CHROME-VANADIUM STEELS**—A sample of 4 or 5 grams is convenient when the percentage of vanadium is low (0.15 to 0.25 per cent). Place it in a 600-cc. beaker, add 30 to 35 cc. of water, and run in a measured volume of sulfuric acid, sp. gr. 1.83, from a buret. Each gram of iron requires 1.5 cc. of concentrated sulfuric acid for final conversion into ferric sulfate. If an excess of 3 or 4 cc. of acid is allowed, the process of solution is rapid. After the steel has been completely decomposed, boil until a considerable quantity of salts separates out, in order to assist in decomposing carbides. Dilute with 20 cc. of water and heat until the salts have dissolved. Add nitric acid, sp. gr. 1.42, drop by drop, to the hot liquid until the violent oxi-



dation of ferrous sulfate is over (3 to 3.5 cc. of acid are sufficient). Boil the solution to destroy oxides of nitrogen, dilute to 200 cc., and add to this solution, which should be at room temperature, 6 cc. of hydrochloric acid, sp. gr. 1.18 (if a 4- or 5-gram sample is used; with a smaller sample more must be added, as given in Table I), 5 grams of ammonium sulfate, and 1.5 to 2 grams of potassium bromate. Leave the material on a low-temperature hot plate for 15 minutes or longer, by which time it should reach approximately 65° C., boil 10 minutes to destroy excess bromate, cool in ice to 5° C., add 25 cc. of ice-cold sulfuric acid, sp. gr. 1.5, and titrate with 0.025 *N* ferrous sulfate.

(2) VANADIUM IN CHROME-VANADIUM-TUNGSTEN STEELS—The sample may conveniently vary from 1.5 grams for a steel containing 1 per cent or more of vanadium to 3 grams for 0.2 per cent vanadium. Add 25 to 30 cc. of water to the sample weighed into a 400-cc. beaker. Use 1.5 cc. of sulfuric acid, sp. gr. 1.83, for each gram of steel and 3 to 6 cc. excess. Warm gently until there is no further evolution of hydrogen. Boil over a free flame until salts begin to separate in order to assist in breaking up carbides, dilute to about 50 cc., and boil until the salts have dissolved. To the boiling hot solution add nitric acid, sp. gr. 1.42, drop by drop, until the violent action is over, then 5 to 6 cc. excess. Boil down until tungstic acid separates out in considerable amount and becomes yellow; dilute somewhat with hot water, let settle, and filter the tungstic acid using hot 1 per cent sulfuric acid to transfer the precipitate to the filter. Place a 150-cc. beaker under the funnel, puncture the paper, and wash through most of the tungstic acid with water. Dissolve the remainder of the material on the filter with hot 4 per cent sodium hydroxide. Add 5 to 10 cc. more to the original beaker to dissolve any precipitate that adheres to the glass, using only about 15 cc. in all. It is convenient to have on hand a stock solution of ferric ammonium alum (345 grams of the salt per liter) of such a strength that 25 cc. of the solution will contain 1 gram of iron and 1 cc. of sulfuric acid, sp. gr. 1.83. To the main filtrate from the tungstic acid, contained in a 600-cc. beaker, add 75 cc. of this stock alum solution (equivalent to 3 grams Fe) and, stirring constantly, pour in the sodium tungstate which will contain some ferric hydroxide in suspension. A clear solution will result, and the volume of liquid at this point should be about 200 cc. Add 6 cc. of hydrochloric acid, sp. gr. 1.18, if a 1.5-gram sample of steel was used, or 4 cc. if a sample larger than 2 grams was taken (see Table I), and 1.5 to 2 grams of potassium bromate. From this point the procedure is similar to that given in (1).

*Note*—For very refractory steels in which it may not be possible to decompose the carbides and completely oxidize the tungsten by dissolving the sample in sulfuric acid and treating with nitric acid, either of the following procedures may be used: (a) The tungstic acid precipitate may be

fused with sodium peroxide in an iron crucible, the melt extracted with hot water, the solution boiled to decompose peroxide, 0.1 gram of sodium sulfite added to reduce any chromate present, and the solution returned to the main filtrate to which additional iron has been added; or (b) hydrochloric acid may be used as the solvent for the steel and nitro-hydrochloric as the oxidizing agent. In this case the directions to be followed are given later in the indicator procedure (4), modifying them by returning the tungstic acid and impurities to the main filtrate, to which additional iron has been added.

### Use of an Internal Indicator

Preliminary experiments with diphenylbenzidine showed that the purple color of the oxidation product of the indicator could be developed rapidly in a solution containing vanadic acid and considerable sulfuric acid, but that the color change at the end point was too slow for practical use. If sufficient sodium acetate was added to react with the free acid in the solution, followed by the indicator, the initial development of the purple color was much slower, but the change at the end point was rapid. When ferric iron was present, it was necessary to add phosphoric acid and sufficient sodium acetate to react with the strong acid other than phosphoric in the solution to obtain a satisfactory end point. After adding the indicator a definite amount of time (5 minutes) should be allowed before the titration is commenced so that the blank correction applied for the indicator will have a constant value. In solutions containing both chromium and iron the greenish purple color of the solution changed to a green or bluish green at the end point. No color is developed in the presence of even a trace of tungstic acid.

The volumes of ferrous sulfate required in a vanadic acid titration when either diphenylbenzidine or diphenylamine was used were compared. Four grams of iron in the form of ferric ammonium alum, 100 mg. of chromium as chromium sulfate, 12 mg. of vanadium as ammonium vanadate solution, 5 cc. of concentrated hydrochloric acid, and 25 cc. of phosphoric acid, sp. gr. 1.37, were diluted to 300 cc. Such a solution would approximate in composition that obtained in a steel analysis after oxidation of the vanadium by the bromate method. Thirty grams of crystallized sodium acetate (trihydrate) were added—slightly more than required to react with the sulfuric acid in the ferric alum and the hydrochloric acid present. This buffered solution represents very closely the solution obtained in a steel analysis after the reduction of chromium by hydrogen peroxide in the Willard and Fenwick method.<sup>6,7</sup> The indicator color was developed in this buffered solution. Table III gives the results for 0.1 per cent solution of diphenylamine and diphenylbenzidine. Ten cubic centimeters of the ammonium vanadate solution required 10.77 cc. of 0.025 *N* ferrous sulfate in an electrometric titration.

The figures in the last column were obtained by calculating the blank for 0.1 cc. of indicator from the volume of

ferrous sulfate required when 1.5 cc. of indicator was used,  $0.45/15 = 0.03$  cc. This correction was applied to the other data in which the volume of indicator was different. A comparison of the values in the last two columns shows that the blank correction for diphenylbenzidine is proportional to the volume of indicator used, and that it is much smaller than for diphenylamine.

**Table III—Results with Diphenylamine and Diphenylbenzidine**

| INDICATOR         | 0.1%<br>INDICATOR | FeSO <sub>4</sub><br>(0.025 N) | ACTUAL<br>BLANK | CALCD.<br>BLANK |
|-------------------|-------------------|--------------------------------|-----------------|-----------------|
|                   | Cc.               | Cc.                            | Cc.             | Cc.             |
| Diphenylamine     | 1.5               | 10.09                          | 0.68            |                 |
|                   | 1.0               | 10.26                          | 0.41            |                 |
| Diphenylbenzidine | 1.5               | 10.32                          | 0.45            | 0.45            |
|                   | 1.0               | 10.46                          | 0.31            | 0.30            |
|                   | 0.8               | 10.55                          | 0.22            | 0.24            |
|                   | 0.6               | 10.60                          | 0.17            | 0.18            |
|                   | 0.4               | 10.65                          | 0.12            | 0.12            |

Other experiments showed that the blank correction for the indicator was independent of a wide variation in iron content or in volume of solution. The amount of acid present was immaterial provided that all acid other than phosphoric was buffered with sodium acetate. No error was involved if the temperature of the solution at the time the indicator was added was between 10° and 40° C. With a higher temperature the error was considerable.

The 0.1 per cent solution of diphenylbenzidine was prepared by dissolving 0.1 gram of the reagent in 10 cc. concentrated sulfuric acid and diluting this with 90 cc. of glacial acetic acid.

### **Analysis of Alloy Steels—Indicator Method**

#### *Recommended Procedure*

(3) **VANADIUM IN CHROME-VANADIUM STEELS**—Follow the directions given in the electrometric procedure (1) through the bromate oxidation process. After the removal of bromate by boiling, add to the solution, cooled to room temperature, 25 cc. of orthophosphoric acid, sp. gr. 1.37, prepared by diluting acid of sp. gr. 1.75 with an equal volume of water, and that quantity of crystallized sodium acetate which is required to react with the excess of sulfuric acid used in dissolving the steel and with the amount of hydrochloric acid which has been used in the method. Too much will cause precipitation of ferric phosphate. (1 cc. of concentrated sulfuric acid is equivalent to 4.8 grams of sodium acetate trihydrate and 1 cc. of concentrated hydrochloric acid to 1.6 grams.) As soon as this has dissolved add 0.6 to 0.8 cc. of 0.1 per cent diphenylbenzidine solution, allow 5 minutes for the color to develop, and titrate with 0.025 *N* ferrous sulfate. The correction to be applied for the indicator is added to the volume of ferrous sulfate and amounts to 0.03 cc. of 0.025 *N* ferrous sulfate per 0.1 cc. of indicator. The end point is very sharp.



## (4) VANADIUM IN CHROME-VANADIUM-TUNGSTEN STEELS—

In steels of this type the tungstic acid must be completely removed because of its effect on the indicator. A 1.5-gram sample is convenient for a steel containing 1 per cent or more of vanadium, and a 2-gram sample for a smaller percentage of vanadium. Add 10 cc. of water and 30 cc. of hydrochloric acid, sp. gr. 1.18, to the sample in a 400-cc. beaker. Warm gently until the steel is completely decomposed and the tungsten separates out as a black powder. To the boiling hot solution add 8 cc. of nitric acid, sp. gr. 1.42, at first cautiously, until the violent action is over. Boil, rotate the liquid frequently to expose a fresh surface of the tungsten to the oxidizing agent, and evaporate to 20 cc. If there are any dark particles in the tungstic acid, add 10 cc. of hydrochloric acid, 3 cc. of nitric acid, and boil down again to 20 cc. To measure this volume, place 20 cc. of water in a beaker of the same size, and boil the filtrate until its volume appears to be equal to that of the water. The volume of hydrochloric acid in this 20 cc. of solution may be considered to be 20 per cent or 4 cc. Dilute to 60–70 cc. with hot water, boil a few moments to dissolve any salts, and let settle on the hot plate until the supernatant liquid is clear.

*Note*—An excellent color development with the indicator was always obtained if this solution was allowed to stand on the hot plate overnight. Such a long period is not necessary, however, for good results.

Filter the tungstic acid through a fine-texture filter paper, using hot 2 per cent hydrochloric acid to transfer the precipitate and to wash it. Note the amount of wash solution used, as the hydrochloric acid in it must be taken into account later. Follow the directions given in the electrometric procedure (2), for dissolving the tungstic acid. Filter this solution into another 150-cc. beaker and set aside for the colorimetric determination of the small amount of vanadium in it. Dilute the filtrate from the tungstic acid to 200 cc., add 5 grams ammonium sulfate, sufficient hydrochloric acid, sp. gr. 1.18, to make 15 cc. in all (the 4 cc. left after boiling down the original solution and the volume present in the amount of 2 per cent wash solution used must be taken into account), which will be a correct amount for a 1.5- or 2-gram sample (Table I), and 1.5–2 grams of potassium bromate. From this point proceed as directed under (3). For this determination 15 cc. of orthophosphoric acid, sp. gr. 1.37, are sufficient and 20 grams of sodium acetate trihydrate. If this causes a precipitate, 2 or 3 drops of sulfuric acid will cause the solution to become clear.

If no purple color develops within 5 minutes after the indicator is added, the tungstic acid has not been completely removed. It is well to set this solution aside for a time. In 30 minutes a deep color may develop and a titration thereby be possible. If care is taken to remove the tungstic acid quantitatively, no difficulty will be encountered.

The small amount of vanadium in the tungstic acid precipitate is determined colorimetrically. To the sodium tungstate solution which has been freed from any suspended matter by filtration and which should approximate 75-100 cc. in volume, add 5 cc. of orthophosphoric acid, sp. gr. 1.37. Compare the yellow solution of vanadotungstic acid within 1 or 2 hours with a standard prepared by adding from a buret a stock solution, containing a known amount of vanadium in the form of vanadotungstic acid, to about 50 cc. of water in a 150-cc. beaker until the intensity of color in the unknown and the standard is the same. The liquids must be of equal volume for this final comparison.

*Preparation of Standard Stock Solution Containing Vanadium*—A solution with 0.1 mg. of vanadium and 5 mg. of tungsten per 1 cc. is convenient. For 500 cc. of such a solution, the required amounts of sodium vanadate and sodium tungstate are dissolved in water, diluted somewhat, 25 cc. of orthophosphoric acid, sp. gr. 1.37, added, followed by water to the final volume. If only ammonium vanadate is available rather than the sodium salt, it should be dissolved in 25 to 30 cc. water, 10 cc. of 4 per cent sodium hydroxide added, and the solution boiled a few minutes to remove all ammonia, the presence of which would cause the formation of insoluble ammonium phosphotungstate later.

#### Summary of Analyses of Steels

The results of vanadium determinations on a number of steels, using the methods described above, are given in Tables IV and V.

Table IV—Vanadium in Chrome-Vanadium Steels

| STEEL                            | BROMATE METHOD |           | PEROXIDE METHOD |           |
|----------------------------------|----------------|-----------|-----------------|-----------|
|                                  | Electrometric  | Indicator | Electrometric   | Indicator |
|                                  | Per cent       | Per cent  | Per cent        | Per cent  |
| B. of S. No. 30 (a)<br>(0.21% V) | 0.206          | 0.201     |                 |           |
|                                  | 0.205          | 0.200     |                 |           |
|                                  | 0.204          | 0.200     |                 |           |
|                                  | 0.206          | 0.201     |                 |           |
| 1                                | 0.230          | 0.227     |                 |           |
|                                  | 0.229          | 0.226     |                 |           |
|                                  | 0.230          | 0.224     |                 |           |
|                                  | 0.230          | 0.223     |                 |           |
| 2                                | 0.216          | 0.212     | 0.211           | 0.215     |
|                                  | 0.220          | 0.214     |                 | 0.216     |

In Table IV 4- to 5-gram samples were used. The results for No. 2 were checked by the peroxide method of Willard and Fenwick.<sup>6</sup>

Experiments with B. of S. steel, No. 72 (0.012 per cent V and 0.149 per cent Mo), to which a known amount of vanadium was added, showed that the bromate method for vanadium was equally applicable to a steel containing molybdenum. Either the electrometric or indicator method could be used for the end point in the vanadic acid titration.

In Table V, 1.0- to 1.5-gram samples were used. The tungsten in the four steels listed varied from 14 per cent to 19 per cent.

Table V—Vanadium in Chrome-Vanadium-Tungsten Steels

| STEEL                         | BROMATE METHOD |           | STEEL | BROMATE METHOD |           |
|-------------------------------|----------------|-----------|-------|----------------|-----------|
|                               | Electrometric  | Indicator |       | Electrometric  | Indicator |
| B. of S. No. 50<br>(0.756% V) | 0.752          | 0.747     | 4     | 1.243          | 1.252     |
|                               | 0.743          | 0.748     |       | 1.224          | 1.259     |
|                               |                | 0.756     |       |                | 1.256     |
| 3                             | 1.817          | 1.826     | 5     | 0.471          | 0.486     |
|                               | 1.823          | 1.828     |       | 0.480          | 0.482     |
|                               |                | 1.830     |       | 0.468          |           |

*Test for Purity of Bromate*—Since chlorate is a common impurity in bromate, it was necessary to know the maximum percentage of this which could be present without preventing the end-point break or causing an appreciable blank. The effect of 0.12 per cent potassium chlorate added to the pure bromate was not harmful as too small an amount of it remained to be detected after 10 minutes' boiling, but 0.25 per cent chlorate caused a blank equivalent to 0.12–0.15 mg. vanadium and made the end-point break extremely poor. The following procedure gave a satisfactory means of testing a supply of bromate: To 200 cc. of water in a 600-cc. beaker, 3 cc. of sulfuric acid, sp. gr. 1.83, 6 cc. of hydrochloric acid, sp. gr. 1.18, 5 grams of ammonium sulfate, and 2 grams of the bromate were added. The solution was boiled vigorously for 10 minutes and then cooled to room temperature. If not more than 3 drops (0.22 cc.) of methyl orange (containing 0.02 gram of the indicator in 100 cc. of solution) will impart a permanent color to this solution, the material is satisfactory for the bromate oxidation method. It was found that for the purest bromate and for two other c. p. samples tested in this way 1 drop (0.07 cc.) of the indicator was required; for the purest material plus 0.12 per cent potassium chlorate, 3 drops.

### Summary

Vanadium is determined without separation from tungsten, chromium, molybdenum, and iron by selective oxidation with bromate in a solution containing ammonium salts and a definite concentration of hydrochloric acid. The excess of bromate is removed by boiling and the vanadic acid titrated electrometrically with ferrous sulfate.

Tungstic acid is kept in solution by dissolving it in sodium hydroxide and pouring it back into the original solution to which sufficient ferric sulfate has been added. In this soluble form it does not interfere.

Diphenylbenzidine, like diphenylamine, is a very satisfactory internal indicator for the titration of vanadic acid with ferrous sulfate. Tungstic acid, even in small amounts, prevents the formation of the indicator color, and therefore must be removed, but molybdenum does not interfere. The small amount of vanadium in the tungstic acid is estimated colorimetrically as yellow vanadotungstic acid by dissolving the tungstic acid in alkali and acidifying this solution with phosphoric acid.



# Persulfate Method for Chromium Plus Vanadium in Chrome-Vanadium-Tungsten Steels

## Modified Procedures

IT HAS been shown in the previous article that a large quantity of tungstic acid, if dissolved in sodium hydroxide, may be added to an acid solution without precipitation, provided that a sufficient amount of ferric salt is present, and in this soluble form causes no interference in the bromate oxidation method for vanadium if the end point in the vanadic acid titration with ferrous sulfate is determined electrometrically. It is obvious that tungsten, thus kept in solution, would probably not interfere either in the persulfate or permanganate oxidation methods for chromium in chrome-vanadium-tungsten or in chrome-tungsten steels. The persulfate method<sup>1,13</sup> was chosen as the simplest and most commonly used, and in the procedure which follows the directions for chromium in the presence of tungsten are given.

### Electrometric End Point

#### *Recommended Procedure*

(1) CHROMIUM IN CHROME-VANADIUM-TUNGSTEN STEELS —A 1- to 1.5-gram sample is convenient. Place it in a 400-cc. beaker, add 40 cc. of water and 10 cc. of sulfuric acid, sp. gr. 1.83. Warm gently until there is no further evolution of hydrogen. Boil over a free flame until salts begin to separate in order to assist in breaking up carbides, dilute to about 50 cc., and boil until the salts have dissolved. To the boiling hot solution add nitric acid, sp. gr. 1.42, drop by drop, until the violent action is over, then 5 to 6 cc. excess. Boil down until tungstic acid separates out in considerable amount; dilute to 60 to 70 cc. with hot water, let settle, and filter off the tungstic acid, using hot 1 per cent sulfuric acid to transfer the precipitate to the filter. Place a 150-cc. beaker under the funnel, puncture the paper, and wash through most of

<sup>13</sup> Lundell, Hoffman, and Bright, *IND. ENG. CHEM.*, **15**, 1064 (1923).

the tungstic acid with water. Dissolve the remainder of the material on the filter with hot 4 per cent sodium hydroxide. Add 5 to 10 cc. more to the original beaker to dissolve any precipitate which adheres to the glass, using only about 15 cc. in all. To the main filtrate from the tungstic acid, contained in a 600-cc. beaker, add 1 gram of iron in the form of ferric alum, and, stirring constantly, pour in the sodium tungstate which will contain some ferric hydroxide in suspension. (It is convenient to have on hand a stock solution of ferric ammonium alum of such strength, 345 grams of the alum per liter, that 25 cc. of the solution will contain 1 gram of Fe and 1 cc.  $\text{H}_2\text{SO}_4$ , sp. gr. 1.83.) A clear solution will result and the liquid should be diluted at this point to 300 cc. Heat to boiling, add 10 cc. silver nitrate containing 2.5 grams  $\text{AgNO}_3$  per liter, and 5 grams of ammonium persulfate. If no permanganate tinge appears in the solution on boiling, a little more persulfate must be added. This difficulty will not be encountered if the correct amounts of sulfuric and nitric acids, as indicated above, are used. Boil the solution for 10 minutes to decompose the excess persulfate. Add 5 cc. 1:3 hydrochloric acid to reduce permanganate and boil vigorously for 10 minutes to remove chlorine. Cool in ice to  $5^\circ \text{C}$ ., add 25 cc. of ice-cold sulfuric acid, sp. gr. 1.5, and titrate the vanadic plus chromic acids electrometrically with 0.1 *N* ferrous sulfate.

In Table VI, 1.0- to 1.5-gram samples were used.

Table VI—Chromium in Chrome-Vanadium-Tungsten Steels—  
Persulfate Oxidation, Electrometric End Point

| STEEL<br>B. of S. No. 50 (3.61% Cr) | CHROMIUM         |
|-------------------------------------|------------------|
|                                     | Per cent         |
| 3                                   | 3.60, 3.55, 3.60 |
| 4                                   | 4.10, 4.11       |
| 4                                   | 3.16, 3.16       |
| 5                                   | 2.83, 2.83       |

#### Use of Indicator

Diphenylbenzidine may be used to determine the end point in the titration of vanadic plus chromic acids with ferrous sulfate in such steels, though the procedure is somewhat longer, provided that the tungstic acid is completely removed, as a very small amount of it interferes with the development of the indicator color. As tungstic acid is not precipitated quantitatively in a sulfuric acid solution, nitrohydrochloric acid must be used, and the filtrate from the tungstic acid evaporated with sulfuric to fumes to remove all hydrochloric acid which would interfere in the oxidation of chromium. The amount of chromium in the tungstic acid is ordinarily small and may be very easily estimated by fusing the tungstic acid with sodium carbonate, extracting with water, filtering, and matching the color of the solution thus obtained with an alkaline solution of equal volume to which standard dichromate is added. For very accurate work it is necessary to estimate the amount of vanadium in the tungstic acid, especially if the steel is high in tungsten and vanadium.

for in such a case considerable vanadium may be retained by the tungstic acid. The procedures for complete removal of the tungstic acid, for the titration of vanadium plus chromium with ferrous sulfate using diphenylbenzidine as indicator (which is the same as that for vanadium with ferrous sulfate), and for the colorimetric estimation of vanadium in tungstic acid are given in the previous article. Furman,<sup>7</sup> who used diphenylamine as an indicator in this same titration, states that the silver chloride must be filtered off as no definite end point can be obtained in its presence. The author has found that silver chloride does not interfere at all with the sharpness of the color change of diphenylbenzidine at the end point, and its removal is therefore unnecessary.

Though the electrometric rather than the indicator method for the end point is preferable in analyzing steels containing tungsten, such is not the case with chrome-vanadium steels. The procedure given below for the indicator method of titrating chromic plus vanadic acids is rapid and accurate, and the color change at the end point is very sharp. The electrometric titration after a persulfate oxidation has been described by Kelley and Conant,<sup>1</sup> and is very satisfactory if the solution is cooled to 5–6° C. at the time of titration. Table VII shows the results for chromium in chrome-vanadium steels.

#### *Recommended Procedure*

(2) CHROMIUM IN CHROME-VANADIUM STEELS—A 2-gram sample is convenient when the steel contains not more than 2 per cent chromium; for samples of larger chromium content a 1-gram sample is suitable. Place it in a 600-cc. beaker, add 15 cc. of water, 15 cc. orthophosphoric acid, sp. gr. 1.37, and run in a measured volume of sulfuric acid, sp. gr. 1.83, from a buret. Allow 1.5 cc. of acid for each gram of steel and 3 cc. excess. After the steel has been completely decomposed, boil until a considerable quantity of salt separates out, in order to assist in decomposing carbides. Dilute with 20 cc. of water and heat until the salts have dissolved. Add nitric acid, sp. gr. 1.42, drop by drop, to the hot liquid until the violent oxidation of ferrous sulfate is over (2 to 3 cc. of acid are sufficient; avoid any appreciable excess). Boil the solution to destroy oxides of nitrogen, dilute to 150 cc., heat to boiling, add 10 cc. of silver nitrate containing 2.5 grams  $\text{AgNO}_3$  per liter, and 1.5 grams of ammonium persulfate. If no permanganate tinge appears in the solution on boiling, add more ammonium persulfate. In no case will more than 2 to 2.5 grams be required if samples of the weights suggested above are used. Boil the solution for 10 minutes to decompose the excess persulfate, dilute to 200 cc., heat to boiling, add 5 cc. of 1:3 hydrochloric acid to reduce permanganate, and boil vigorously for 10 minutes to remove chlorine. Add to the solution at room temperature



that quantity of crystallized sodium acetate which is required to react with the excess of sulfuric acid used in dissolving the steel. (1 cc. of concentrated sulfuric acid is equivalent to 4.8 grams of sodium acetate trihydrate.) As soon as this has dissolved, add 0.6 to 0.8 cc. of 0.1 per cent diphenylbenzidine solution (prepared by dissolving 0.1 gram of the reagent in 10 cc. of concentrated sulfuric acid and diluting this with 90 cc. of glacial acetic acid), allow 5 minutes for the color to develop, and titrate with 0.05 *N* ferrous sulfate. The correction to be applied for the indicator is added to the volume of ferrous sulfate and amounts to 0.015 cc. of 0.05 *N* ferrous sulfate per 0.1 cc. of indicator.

In Table VII, 1.5- to 2-gram samples were used.

Table VII—Chromium in Chrome-Vanadium Steels—Persulfate Method

| STEEL                          | CHROMIUM        |                 |
|--------------------------------|-----------------|-----------------|
|                                | Electrometric   | Indicator       |
|                                | <i>Per cent</i> | <i>Per cent</i> |
| B. of S. No. 30 (a) (1.02% Cr) | 1.03            | 1.02            |
|                                | 1.03            | 1.02            |
|                                | 1.04            | 1.04            |
| 1                              | 2.34            | 2.33            |
|                                | 2.34            | 2.34            |
|                                | 2.34            |                 |
| B. of S. No. 72 (0.91% Cr)     |                 | 0.91            |
|                                |                 | 0.91            |

### Summary

Two modified procedures of the persulfate method for determining the sum of chromium and vanadium in special alloy steels have been developed:

1. In a chrome-vanadium-tungsten or a chrome-tungsten steel tungstic acid is kept in solution by dissolving it in sodium hydroxide and pouring it back into the original solution to which additional ferric sulfate has been added. The oxidation of the chromic and vanadyl salt by persulfate and the electrometric titration with ferrous sulfate may be carried out in the presence of this soluble tungstic acid.

2. In a chrome-vanadium steel the sum of chromium and vanadium obtained by a persulfate oxidation may be determined by titration with standard ferrous sulfate, using diphenylbenzidine as an internal indicator.

•

## PART II

### CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT

- I. The Preparation and Standardization of Solutions. The Determination of Calcium.
- II. The Determination of Iron.
- III. The Titration of Iodide.
- IV. The Determination of Arsenic.
- V. The Determination of Antimony.
- VI. The Volumetric Determination of Cerium.
- VII. The Determination of Vanadium in the Presence of Chromium, Tungsten and Iron.
- VIII. The Determination of Chromium in the Presence of Manganese, Iron and Vanadium.
- IX. The Preparation and Stability of Solutions.

## I. THE PREPARATION AND STANDARDIZATION OF SOLUTIONS. DETERMINATION OF CALCIUM

### Introduction

The use of ceric salts as oxidizing agents has been suggested by a number of authors. Lange<sup>1</sup> in referring to the oxidizing properties of ceric sulfate recommends it as a volumetric reagent; Sonnenschein<sup>2</sup> suggests it instead of permanganate for the titration of iron; A. Job<sup>3</sup> speaks of the stability and strong oxidizing properties of acid solutions of ceric salts and of their possible use in cases where permanganate is not applicable as in the estimation of oxalochlorides, the excess of the reagent being determined with hydrogen peroxide. This last author states that the oxidizing solution may be prepared from ordinary commercial cerium compounds as the presence of the other monazite metals has no influence on results. G. Barbieri<sup>4</sup> discusses the volumetric determination of nitrous acid by means of tetravalent cerium, the factor of which is determined iodimetrically or with hydrogen peroxide. He remarks that ceric compounds are reduced by hydrazine and hydroxylamine salts in the cold. Sommer and Pincas<sup>5</sup> find that salts of quadrivalent cerium immediately effect the complete oxidation of hydrazoic acid in neutral or acid solution, and Martin<sup>6</sup> has developed an iodimetric method for determining the excess of ceric sulfate used in this oxidation. Benrath and Ruland,<sup>7</sup> in a paper on the oxidizing action of ceric sulfate, discuss the oxidation of a number of organic compounds as tartaric acid, oxalic acid, anthracene, hydrazine, hydroxylamine, as well as sodium thiosulfate, sulfurous acid, hypophosphorous acid. Ceric salts have been used in the electrolytic oxidation of organic compounds and a number of volumetric methods for the estimation of cerium have been worked out.<sup>8</sup> No one, however, has yet used ceric salts in the direct titration of reducing agents.<sup>9</sup>

<sup>1</sup> Lange, *J. prakt. Chem.*, **82**, 129 (1861)

<sup>2</sup> Sonnenschein, *Ber.*, **3**, 631 (1870).

<sup>3</sup> Job, *Compt. rend.*, **128**, 101 (1899).

<sup>4</sup> Barbieri, *Chem.-Ztg.*, **29**, 668 (1905).

<sup>5</sup> Sommer and Pincas, *Ber.*, **48**, 1963 (1915).

<sup>6</sup> Martin, *J. A. C. S.*, **49**, 2133 (1927).

<sup>7</sup> Benrath and Ruland, *Z. anorg. allgem. Chem.*, **114**, 267 (1920).

<sup>8</sup> Lessing, *Z. anal. Chem.*, **71**, 161 (1927), gives a brief summary of the methods for cerium.

<sup>9</sup> After this material was submitted for publication, a paper appeared by Fur-

An extensive development of analytical methods based upon the use of ceric salts as volumetric reagents would have been difficult before the advent of the potentiometric method of determining an end-point. Though a visual change or an internal indicator may be used in some cases, the end-point in many of the titrations must be determined electrometrically. Since the oxidation potential of the most powerful oxidizing agents such as that of permanganate in acid solution is very close to that of ceric compounds in a similar medium,<sup>10</sup> the latter should prove to be very strong oxidizing agents and should behave in many reactions in a manner similar to permanganate. A ceric salt has, however, one great advantage, namely, that only trivalent cerium can be formed in its reduction, whereas with permanganate several reduction products are possible and it is not always easy to avoid the formation of more than one of these in a given reaction. Ceric salts may be used in solutions containing a high concentration of hydrochloric acid and are very stable toward heat, while the use of permanganate under such conditions is almost always out of the question. The author has therefore made a systematic study of ceric salts as oxidizing agents in volumetric analysis.

## Experimental

### Preparation of Ceric Sulfate

The supply of U. S. P. cerous oxalate available was found by Metzger's bismuthate method<sup>11</sup> to contain 48.22% of  $\text{CeO}_2$  in the ignited oxide. While a pure cerium compound was not necessary for this work because no interference from the other rare earths was to be expected, it seemed better to use material containing a higher percentage of cerium. On the other hand, a material not too pure has certain advantages: a mixed oxide of the rare earths containing about 85% of  $\text{CeO}_2$  is attacked readily by sulfuric acid, sp. gr. 1.5, with the formation of ceric sulfate, while a very pure sample of  $\text{CeO}_2$  must be treated with concentrated sulfuric acid to obtain the sulfate.<sup>12</sup> The pure oxide is a relatively expensive reagent, but a ceric oxide containing other rare earths is inexpensive.

A slight modification of Roberts' permanganate process<sup>13</sup> for concentrating cerium in a rare earth mixture was used. The solution of the nitrates, diluted considerably with water, was heated to boiling, stirred mechanically and treated with sodium carbonate solution until a slight permanent precipitate was formed. This was dissolved in nitric acid, added drop by drop, and to the boiling hot liquid a solution, 0.25 molar in potassium permanganate and 1 molar in sodium carbonate, was added until a fair excess of permanganate was present. By this procedure all of the cerium was precipitated as dioxide

man, *J. A. C. S.*, **50**, 755 (1928), in which he showed that ceric sulfate could be standardized against oxalate or ferrous sulfate in sulfuric acid solution. The author's results confirm the accuracy of these methods and considerably extend the usefulness of these reactions.

<sup>10</sup> Tomiček, *Rec. trav. chim.*, **44**, 410 (1925).

<sup>11</sup> Metzger, *J. A. C. S.*, **31**, 523 (1909).

<sup>12</sup> Meyer and Aufrecht, *Ber.*, **37**, 140 (1904); Spencer, *J. Chem. Soc.*, **107**, 1265 (1915).

<sup>13</sup> Roberts, *Am. J. Sci.*, [IV] **31**, 350 (1911).



along with some of the other rare earth oxides. Roberts' directions were followed in converting these oxides into chlorides and subsequently into oxalates. A considerable quantity of material was worked up by this method and the chloride solutions were combined and stirred thoroughly so that the entire oxalate precipitate would be of the same composition. The ignited oxides from this oxalate contained 85.1% of  $\text{CeO}_2$ . When the oxalate was ignited at 600–625° for ten hours, slightly more than 99% of the cerium in it was converted into  $\text{CeO}_2$ . If this was dissolved in sulfuric acid, sp. gr. 1.5, diluted and titrated directly for ceric content, 91.2% of the  $\text{CeO}_2$  in the oxide was found as ceric sulfate. While the conversion into oxide was more nearly complete at a higher temperature, the yield of ceric salt was somewhat lower.

To prepare a large amount of ceric sulfate solution, portions of the oxide, ignited at 600–625°, were treated with sufficient sulfuric acid, sp. gr. 1.5, to make the final solution 0.5 or 1 molar in acid when it was diluted sufficiently to give a 0.1 *N* ceric sulfate solution. This oxide-acid mixture was kept at 125–130° and stirred mechanically until the pale pinkish brown oxide, which was converted first into a deep red material, became a bright yellow in color. This material was diluted almost to the volume required for a 0.1 *N* solution and kept at 75–80° for an hour while being stirred mechanically. It was filtered hot from the small amount of undissolved material, which appeared to be unchanged  $\text{CeO}_2$  and was combined with similar precipitates to be worked up later. If the U. S. P. oxalate was ignited, this impure oxide dissolved readily in sulfuric acid of sp. gr. 1.3.

Some of this ignited oxide was treated with 95% sulfuric acid at a temperature of 150–155°, and was converted fairly rapidly into the bright yellow ceric sulfate. This, when cool, was added slowly to water at room temperature. Nearly all of the solid dissolved and the actual yield in ceric sulfate from a given weight of the ignited oxide was very nearly the same as that in the process described above. The first method was somewhat more convenient.

A further supply of 0.1 *N* ceric sulfate was made from c. p.  $\text{CeO}_2$ , very pale yellow in color, by treatment with concentrated sulfuric acid as described above. From the strength of the solution obtained, it was found that 98.2% of the oxide used in the process was converted into ceric sulfate.

During a three months' interval, the normality factor of this ceric sulfate solution was constant to within one part in a thousand.

Different cerium compounds were used to prepare 0.1 *N* ceric sulfate, the purpose being to compare the cost of a liter of these solutions. Pure ceric sulfate and pure ceric ammonium nitrate, converted into sulfate by evaporation with sulfuric acid, were out of the question because of the expense. The approximate cost of the cerium compound for a liter of 0.1 *N* solution from c. p.  $\text{CeO}_2$  was eighty-five cents, from U. S. P. cerous oxalate ten cents. While this last material is satisfactory for the preparation of such a volumetric solution, an oxalate containing 80–85% of the theoretical quantity of  $\text{CeO}_2$  is perhaps preferable.

### Standardization of Ceric Sulfate

Since it is very desirable to use a primary standard for this purpose, a study was made of the titration of sodium oxalate in hot solution with ceric sulfate, the reaction being



Portions of a standard solution of sodium oxalate from the U. S. Bureau of Standards were acidified with sulfuric acid, heated nearly to boiling and titrated electrometrically with 0.1 *N* ceric sulfate prepared from the ignited

oxide containing 85.1% of  $\text{CeO}_2$ . Two cc. of sulfuric acid was contained in the ceric sulfate used. In all of this work a silver chloride-platinum electrode system was used. The silver chloride electrode in 0.1 *N* potassium chloride was placed directly in the liquid to be titrated. The results are shown in Table I.

These data indicate that concordant results may be obtained when the volume of the solution is varied from 100–300 cc. (larger variations in volume were not studied) and when the weight of sodium oxalate is changed over wide limits. The end-point reaction is quite rapid if not more than 2.5 cc. of concd. sulfuric acid is present per 100 cc. of solution at the time of titration. The high result obtained in the last experiment is probably due to the low acid content of the solution. No acid was added before the titration and only 1.85 g. of sulfuric acid was present in the ceric sulfate. It is probable that not quite all of the cerous oxalate was dissolved. In the other experiments in which no acid was added, a considerable quantity of cerous oxalate precipitated on the addition of the first portion of ceric sulfate and then dissolved as more of the reagent was added.

TABLE I  
EFFECT OF SULFURIC ACID

| $\text{Na}_2\text{C}_2\text{O}_4$ ,<br>g. | Initial vol.,<br>cc. | $\text{H}_2\text{SO}_4$ , sp.<br>gr. 1.83, at<br>beginning, cc. | $\text{Ce}(\text{SO}_4)_2$ ,<br>normality | Character of<br>end-point |
|-------------------------------------------|----------------------|-----------------------------------------------------------------|-------------------------------------------|---------------------------|
| 0.2679                                    | 200                  | 0                                                               | 0.1067                                    | Rapid                     |
| .2679                                     | 200                  | 5                                                               | .1067                                     | Fairly rapid              |
| .2679                                     | 200                  | 10                                                              | .1067                                     | Slow                      |
| .2679                                     | 300                  | 0                                                               | .1067                                     | Rapid                     |
| .2679                                     | 300                  | 7.5                                                             | .1068                                     | Fairly rapid              |
| .2679                                     | 300                  | 15                                                              | .1068                                     | Slow                      |
| .2679                                     | 100                  | 0                                                               | .1067                                     | Rapid                     |
| .2679                                     | 100                  | 2.5                                                             | .1067                                     | Slow but usable           |
| .2679                                     | 100                  | 5                                                               | .1068                                     | Too slow                  |
| .1339                                     | 300                  | 7.5                                                             | .1067                                     | Rapid                     |
| .5358                                     | 300                  | 0                                                               | .1067                                     | Rapid                     |
| .1339                                     | 300                  | 0                                                               | .1081                                     | Fairly rapid              |

Experiments showed that the equilibrium at the end-point was reached too slowly in all cases if the temperature of the solution at the end of a titration was below 70°. At or above this temperature results were as indicated in Table I.

The results were identical no matter whether the ceric sulfate solution was added slowly to the oxalate, as would be necessary in a permanganate titration, or rapidly from a pipet.

Portions of a standard solution of sodium oxalate were acidified with hydrochloric acid, heated nearly to boiling and titrated electrometrically with 0.1 *N* ceric sulfate. The reaction at the end-point was rapid in all cases. The results are shown in Table II.

TABLE II  
EFFECT OF HYDROCHLORIC ACID

| $\text{Na}_2\text{C}_2\text{O}_4$ ,<br>g. | Initial vol.,<br>cc. | $\text{HCl}$ , sp. gr. 1.18,<br>at beginning, cc. | $\text{Ce}(\text{SO}_4)_2$ ,<br>normality |
|-------------------------------------------|----------------------|---------------------------------------------------|-------------------------------------------|
| 0.2679                                    | 200                  | 0                                                 | 0.1043                                    |
| .2679                                     | 200                  | 5                                                 | .1043                                     |
| .2679                                     | 200                  | 20                                                | .1042                                     |
| .2679                                     | 200                  | 40                                                | .1043                                     |
| .2679                                     | 200                  | 60                                                | .1043                                     |
| .2679                                     | 100                  | 10                                                | .1042                                     |
| .2679                                     | 300                  | 30                                                | .1042                                     |
| .1339                                     | 300                  | 30                                                | .1041                                     |
| .5358                                     | 300                  | 30                                                | .1043                                     |

It is seen that ceric sulfate may be used with no special precautions in strong hydrochloric acid solutions and thus has a decided advantage over permanganate. The end-point break in the above experiments averaged about 175–200 mv. per 0.02 cc. of 0.1 *N* ceric sulfate, and fifteen minutes after the completion of a titration not the slightest decrease in potential had occurred.

Experiments similar to those made in Tables I and II showed that as much as 60 cc. of 73% perchloric acid or 50 cc. of glacial acetic acid per 200 cc. of solution could be used instead of sulfuric or hydrochloric acid and the end-point reaction was rapid. The presence of even 5 cc. of concd. nitric acid in this same volume however, gave too high a value for the ceric sulfate, showing that this acid had a slight effect on the oxalate. Phosphoric and hydrofluoric acids must be absent, even if considerable hydrochloric acid is present, as they cause the formation of insoluble cerium salts. In the titration of ferrous ion in hydrochloric acid solution with ceric sulfate, which is described later, the presence of a moderate amount of phosphoric acid causes no interference, probably because this reaction is a more rapid one than the oxalate–ceric sulfate reaction. Experiments using ceric sulfate solution prepared from pure  $\text{CeO}_2$  gave the same results.

Since in the titration of oxalate the solution is colorless until an excess of ceric sulfate is present, the possibility of using a visual end-point was investigated. An initial volume of 200 cc., containing 10–20 cc. of concd. hydrochloric acid, was used. If an equal volume of water is taken as a comparison liquid, the slightest change in color at the end-point is easily seen. A blank determination made at 70° on 200 cc. of water containing 20 cc. of concd. hydrochloric acid and 3–5 cc. of concd. sulfuric acid (the volume in the ceric sulfate added) showed that 0.05 cc. of 0.1 *N* ceric sulfate was required to give a pale yellow color. Unless sulfuric acid was added, the ceric sulfate was reduced. When this amount was subtracted from the volume of ceric sulfate used in a titration the normality corresponded exactly to that obtained electrometrically.

Quantitative results were obtained in the reverse titration of ceric sul-

fate with sodium oxalate in hot solution when as much as 5 cc. of concd. sulfuric acid was present per 200 cc. of solution. If more sulfuric acid was used, the reaction at the end-point was too slow. Twenty-five cc. of perchloric acid (73%) or 5–20 cc. of concd. nitric acid in the same volume gave quantitative results with a fairly rapid end-point reaction. Hydrochloric acid had a reducing effect on the ceric sulfate present in the hot solution. The end-point breaks amounted to 150–200 mv. per 0.03 cc. of 0.1 *N* sodium oxalate except in the nitric acid solutions where they were of about half this magnitude. It was found that this electrometric titration with oxalate could be used after a bismuthate oxidation,<sup>11</sup> but the equilibrium in the region of the end-point was quite slow, due to the large amount of acid present.

### Iodine Chloride as Catalyst

Later work which showed the value of certain iodine compounds as catalyst in the reaction between arsenite and ceric salt<sup>14</sup> suggested the possibility of titrating oxalate at room temperature in the presence of such a catalyst. It was found that the titration of oxalate in hydrochloric acid solution containing iodine chloride proceeded rapidly and quantitatively at room temperature. Iodine chloride was chosen although iodide or iodate worked equally well, because it necessitated no blank correction in the volume of ceric sulfate used, since the final form of the catalyst in all cases was iodine chloride. The catalytic action of iodide or iodate seemed a little slower than that of iodine chloride and the blank required for either was an objection.

The action of the catalyst in this reaction is not clear. It was found that iodine chloride is not reduced at all by oxalate in hydrochloric acid solution in thirty minutes, nor does it catalyze at room temperature the action of oxalate in hydrochloric acid solution with (1) potassium permanganate, (2) potassium dichromate or (3) potassium iodate. Its catalytic action seems to be confined to the ceric salt titration and this suggests the possibility that the ceric ion is an important factor, since cerous salt was found not to catalyze the action between iodine chloride and oxalate. This same conclusion was drawn from work with the arsenite titration. This subject is being investigated.

The iodine chloride solution was prepared by dissolving 0.279 g. of potassium iodide and 0.178 g. of potassium iodate in 250 cc. of water and adding all at once 250 cc. of concd. hydrochloric acid.<sup>15</sup> The solution thus obtained was 0.005 *M* in iodine chloride. It was adjusted electrometrically by adding the proper amount of dilute potassium iodide or iodate.

<sup>14</sup> This Dissertation, page 48.

<sup>15</sup> G. S. Jamieson, "Volumetric Iodate Methods," The Chemical Catalog Company, New York, 1926, pp. 8, 9.



Measured portions of a standard solution of sodium oxalate were acidified with hydrochloric acid. Iodine chloride was added and water to a total volume of 100 cc. The end-point was determined electrometrically. The results are shown in Table III.

TABLE III  
TITRATION OF OXALATE, IODINE CHLORIDE AS CATALYST

| $\text{Na}_2\text{C}_2\text{O}_4$ ,<br>0.1 N, cc. | HCl, sp.<br>gr. 1.18, at<br>beginning, cc. | ICl,<br>cc.                   | $\text{Ce}(\text{SO}_4)_2$ ,<br>0.1 N, cc. | Character of<br>end-point |
|---------------------------------------------------|--------------------------------------------|-------------------------------|--------------------------------------------|---------------------------|
| 10                                                | 10                                         | 10                            | 9.98                                       | Slow                      |
| 10                                                | 15                                         | 10                            | 9.99                                       | Rapid                     |
| 10                                                | 25                                         | 10                            | 9.98                                       | Rapid                     |
| 10                                                | 20                                         | 5                             | 9.99                                       | Rapid                     |
| 10                                                | 15                                         | 20                            | 9.99                                       | Rapid                     |
| 50                                                | 15                                         | 10                            | 49.94                                      | Rapid                     |
| 50                                                | 25                                         | 10                            | 49.90                                      | Slow                      |
| 10                                                | 20                                         | 10 cc. 0.0025 M KI            | 10.49                                      | Rapid                     |
| 10                                                | 15                                         | 5 cc. 0.0025 M $\text{KIO}_3$ | 9.54                                       | Fairly slow               |

In the lower acid range (first experiment) the reaction is at first more rapid than in the higher acid range (third experiment), but the reaction at the end point is slower. The addition of 15–25 cc. of concd. hydrochloric acid per 100 cc. of solution, not considering the acid present in the iodine chloride solution, gives the most favorable conditions for a titration. The values of the blanks in the last two experiments, +0.49 cc. and -0.46 cc., correspond very closely with the volumes of ceric sulfate theoretically required, +0.48 cc. and -0.46 cc., to convert either of the catalysts used into iodine chloride. The potential at the beginning of a titration is approximately 625–675 mv., but drops to 400–450 mv. during the addition of the first few cubic centimeters of oxidizing solution. At the end-point the break in potential averaged 200–250 mv. per 0.03 cc. of 0.1 N ceric sulfate.

Methylene blue has been proposed by Sinnatt<sup>16</sup> instead of starch in iodimetric titrations, and Attack<sup>17</sup> has discussed its use as a volumetric reagent in oxidation-reduction reactions. This dye was found to give an excellent end-point in the titration of oxalate with ceric salt in the presence of iodine chloride as catalyst, provided that certain rather narrow experimental conditions were maintained.

During this titration the solution is pale yellow, and as the end-point is approached becomes a deeper yellow, due to the presence of free iodine. As the last portion of ceric sulfate (0.2–0.3 cc.) converts this into iodine chloride, the yellow color gradually fades out. In a titration in which the end-point reaction is rather slow, the electrometric break in potential is indicated when the solution is still somewhat yellow and two or three

<sup>16</sup> Sinnatt, *Analyst*, **35**, 309 (1910); **37**, 252 (1912).

<sup>17</sup> Attack, *J. Soc. Dyers and Colourists*, **31**, 183 (1915).

minutes or longer may be required for this color to bleach out. The color disappears much more quickly when conditions are such that the end-point reaction is rapid. Experiments have shown that methylene blue cannot be added until within 0.4 cc. of the end-point, and the color change is much sharper if it is not added until within 0.2–0.3 cc. Therefore conditions for a rapid end-point reaction must be chosen. When 2 drops of the indicator are added to a pale yellow solution, the solution turns green, and with each succeeding drop of ceric sulfate becomes more blue until a final drop or two of the oxidizing agent causes the whole liquid to turn a deep pink color, which in five to ten seconds changes to a permanent blue shade. Under some conditions the entire solution will not become pink, in which cases, as well as in the above, the end-point is taken as the reading for the last drop which caused the appearance of any pink color in the solution.

Measured portions of a standard solution of sodium oxalate were taken. Iodine chloride and hydrochloric acid were used after sufficient water had been added to make the total volume of the solution 100 cc. at the time of titration. Two drops of a 0.1% solution of methylene blue in water were added when within 0.2–0.3 cc. of the end-point. The results are shown in Table IV.

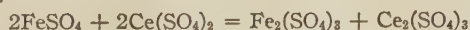
TABLE IV  
TITRATION OF OXALATE—METHYLENE BLUE INDICATOR

| $\text{Na}_2\text{C}_2\text{O}_4$ ,<br>0.1 <i>N</i> , cc. | $\text{HCl}$ , sp. gr. 1.18,<br>at beginning, cc. | $\text{Ce}(\text{SO}_4)_2$ ,<br>0.1 <i>N</i> , cc. | Character of end-<br>point color change |
|-----------------------------------------------------------|---------------------------------------------------|----------------------------------------------------|-----------------------------------------|
| 10                                                        | 15                                                | 10.01                                              | Satisfactory                            |
| 10                                                        | 20                                                | 9.98                                               | Excellent                               |
| 10                                                        | 25                                                | 9.99                                               | Excellent                               |
| 10                                                        | 35                                                | ?                                                  | Not satisfactory                        |
| 25                                                        | 10                                                | 24.99                                              | Fairly satisfactory                     |
| 25                                                        | 15                                                | 24.97                                              | Satisfactory                            |
| 25                                                        | 20                                                | 24.99                                              | Excellent                               |
| 25                                                        | 25                                                | ?                                                  | Not satisfactory                        |
| 50                                                        | 20                                                | 49.83                                              | Satisfactory                            |
| 50                                                        | 15                                                | 49.90                                              | Excellent                               |

The amount of iodine chloride was varied, but 10 cc. was found to give the best results.

#### Titration of Ferrous Iron with Ceric Sulfate

To be able to compare the titrations of ceric sulfate against (1) oxalate and (2) ferrous sulfate as a further check on this method of standardizing a ceric salt, the conditions necessary for the ferrous iron–ceric salt reaction were determined.



The same volume of ceric sulfate was required in each of 6 titrations of 40 cc. of 0.1 *N* ferrous sulfate in which the volume was varied from

100–300 cc. and the sulfuric acid, sp. gr. 1.83, from 0–25 cc. per 100 cc. of solution. The end-point was determined electrometrically; the end-point reaction was rapid in every case and the break in potential amounted to 250–300 mv. per 0.02 cc. of 0.1 *N* ceric sulfate.

Similar results were obtained when hydrochloric or perchloric acid was used. With as much as 40 cc. of concd. hydrochloric acid or 40 cc. of perchloric acid (73%) per 100 cc. of solution, the end-point reaction was rapid and the break in potential large. Nitric acid, however, was detrimental, and the presence of 5 cc. of it per 100 cc. of solution caused a decided decrease in the volume of ceric salt used.

The titration of ceric salt with ferrous sulfate<sup>18</sup> went smoothly when considerable sulfuric or perchloric acid was present. Five cc. of concd. hydrochloric acid per 100 cc. of solution containing 25 cc. of 0.1 *N* ceric sulfate caused no interference if the titration was made without delay. If the solution was allowed to stand for five to fifteen minutes before titration, the reducing action of the acid became evident. Quantitative results were obtained with the use of as much as 30 cc. of concd. nitric acid per 100 cc. of solution.

#### Comparison of Standardizations against Oxalate and Iron

A weight buret was used for the ceric sulfate solution. The samples of sodium oxalate were from the Bureau of Standards and the impurities in the electrolytic iron had been accurately determined. In the titrations of oxalate, in one series, 0.35–0.40-g. samples were dissolved in 200 cc. of water, 10 cc. of concd. hydrochloric acid added and the solutions heated nearly to boiling before titration; while in the second series the samples were dissolved in 75 cc. of water, 15 cc. of concd. hydrochloric acid and 10 cc. of iodine chloride added before titration. In the third series, the samples of electrolytic iron were dissolved in hydrochloric acid, any ferric chloride reduced with a slight excess of stannous chloride, the cooled solution diluted to 150 cc., 10 cc. of saturated mercuric chloride solution added and the solution titrated.<sup>19</sup> The electrometric method was used in all cases. During the titration an atmosphere of carbon dioxide was maintained above the solution to prevent any oxidation of the ferrous iron by air. Later work showed that if this precaution was not taken there was an error of approximately one part in a thousand.

Fig. I shows typical curves for the titration of oxalate and of ferrous iron with ceric sulfate. The results are expressed in terms of a platinum–1*N* calomel electrode system.

<sup>18</sup> Since the completion of this work an article by Someya, *Z. anorg. allgem. Chem.*, **168**, 56 (1927), has appeared in which the electrometric titration of ceric sulfate with ferrous sulfate is described. Also, see reference 9.

<sup>19</sup> The stannous chloride reduction method for iron followed by titration with ceric sulfate is described on pages 38 and 39 of this dissertation.

TABLE V

| WEIGHT NORMALITY OF CERIC SULFATE BY DIFFERENT METHODS |                                                       |                                                                                      |
|--------------------------------------------------------|-------------------------------------------------------|--------------------------------------------------------------------------------------|
| Against (1) Electrolytic Fe,<br>99.97% Fe              | (2) $\text{Na}_2\text{C}_2\text{O}_4$ in<br>hot soln. | (3) $\text{Na}_2\text{C}_2\text{O}_4$ at room temp.<br>with $\text{ICl}$ as catalyst |
| 0.09410                                                | 0.09410                                               | 0.09406                                                                              |
| .09414                                                 | .09416                                                | .09409                                                                               |
| .09408                                                 | .09407                                                | .09409                                                                               |
| .09409                                                 | .09406                                                | .09404                                                                               |
| Average = .09410                                       | .09410                                                | .09407                                                                               |

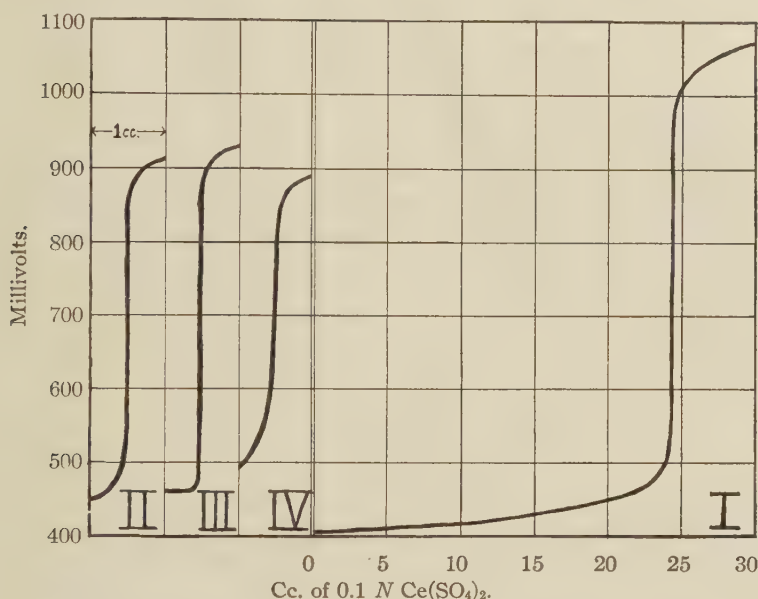


Fig. I.—Curve I.—25 cc. of 0.1  $\text{N Na}_2\text{C}_2\text{O}_4$  titrated with 0.1  $\text{N Ce}(\text{SO}_4)_2$ ; 3 cc. of concd.  $\text{H}_2\text{SO}_4$  in initial vol. of 200 cc. Curve II.—End-point in titration of 0.1  $\text{N FeSO}_4$  with 0.1  $\text{N Ce}(\text{SO}_4)_2$ ; 15 cc. of concd.  $\text{HCl}$  in initial vol. of 100 cc. Curve III.—End-point in titration of 0.1  $\text{N Na}_2\text{C}_2\text{O}_4$  with 0.1  $\text{N Ce}(\text{SO}_4)_2$ ; 15 cc. of concd.  $\text{HCl}$  in initial vol. of 200 cc. Curve IV.—Same as III but 10 cc. of 0.005  $\text{M ICl}$  added.

### Determination of Calcium with Ceric Sulfate

It is obviously possible to use ceric sulfate like permanganate for the volumetric determination of calcium. A. Job<sup>3</sup> has referred to the estimation of oxalic acid in oxalochlorides by addition of excess of ceric salt solution, the excess being determined with hydrogen peroxide, but he gives no experimental data. Benrath and Ruland<sup>7</sup> in a study of the oxidizing action of ceric sulfate state that oxalic acid is oxidized to carbon dioxide and that sulfuric acid and normal sulfates retard the reaction. Since the gravimetric determination of calcium oxide by precipitation as



oxalate and ignition in air at 475–550° to carbonate<sup>20</sup> is a very accurate method, the results obtained in this way were compared with those obtained by volumetric titration with ceric sulfate.

In the following analyses the standard procedure of neutralizing with ammonia a hydrochloric acid solution containing calcium and oxalate ions was followed. The precipitate was collected in a filtering crucible and ignited to carbonate in a muffle at 500–525°. In the volumetric method the precipitate was washed into a beaker with water and the paper then washed thoroughly with dilute hydrochloric acid (60 cc. of water + 10 cc. of HCl) and finally with water. The solution was diluted to 200 cc., heated nearly to boiling and titrated either electrometrically or to a visual end-point with ceric sulfate which had been standardized electrometrically against sodium oxalate. Iodine chloride was not used as a catalyst, though such a method would be equally applicable.

TABLE VI  
SUMMARY OF ANALYSES FOR CALCIUM OXIDE

| Sample         | Percentage of CaO                                                 |        |                               |
|----------------|-------------------------------------------------------------------|--------|-------------------------------|
|                | Titration with Ce(SO <sub>4</sub> ) <sub>2</sub><br>Electrometric | Visual | Weighing as CaCO <sub>3</sub> |
| 1 Iceland Spar | 55.93                                                             | 55.96  | 55.97                         |
|                | 55.92                                                             | 55.93  | 55.99                         |
|                | 55.93                                                             | 55.94  | 56.00                         |
|                |                                                                   |        |                               |
|                | Average                                                           | 55.93  | 55.94                         |
| 2              | 26.60                                                             | 26.64  | 26.65 <sup>a</sup>            |
|                | 26.59                                                             | 26.62  | ...                           |
|                | 26.66                                                             | ...    | ...                           |
|                | 26.60                                                             | ...    | ...                           |
|                | Average                                                           | 26.61  | 26.63                         |
| 3              | 20.00                                                             | 19.94  | 19.94 <sup>a</sup>            |
|                | 19.97                                                             | 20.01  | ...                           |
|                | 20.03                                                             | ...    | ...                           |
|                |                                                                   |        |                               |
|                | Average                                                           | 20.00  | 19.97                         |

<sup>a</sup> These values represent an average of accurate analyses made gravimetrically by another person.

### Summary

1. A solution of ceric sulfate is easily prepared by dissolving in sulfuric acid CeO<sub>2</sub> obtained by igniting the oxalate. Pure material is not necessary as the other rare earths do not interfere in oxidation-reduction reactions.

2. This reagent is in some cases a stronger oxidizing agent than permanganate in acid solution and has a number of advantages over the latter: first, only one valence change is possible, namely, from Ce<sup>++++</sup> → Ce<sup>+++</sup>; second, it may be used in a solution containing a high concentra-

<sup>20</sup> A method tested in this Laboratory but not yet published.

tion of hydrochloric acid; and third, it is very stable toward heat. The normality factor of the solution remains constant over a long period.

3. Ceric sulfate may be accurately standardized against sodium oxalate in hot sulfuric, hydrochloric or perchloric acid solution, the end-point being determined either electrometrically or visually by a change from colorless to yellow. The titration of ceric salt with oxalate is quantitative in hot sulfuric, perchloric or nitric acid solution.

4. The oxalate titration with ceric sulfate may be carried out with the same accuracy at room temperature by the use of iodine chloride as catalyst. The end-point is determined either electrometrically or with methylene blue as internal indicator.

5. Ferrous iron may be determined volumetrically in sulfuric, hydrochloric or perchloric acid solution with ceric sulfate. The reverse titration proceeds quantitatively in a sulfuric, perchloric or nitric acid solution.

6. A method for calcium has been developed, based upon precipitation as oxalate, solution in hydrochloric acid and titration with standard ceric sulfate.

## II. THE DETERMINATION OF IRON

The possibility of titrating ferrous iron with ceric sulfate has been investigated by the author<sup>21</sup> and has been found to give quantitative results in either hydrochloric, sulfuric or perchloric acid solution. Furman<sup>9</sup> has also studied this reaction in sulfuric acid solution. It seemed important to study the application of this titration to the analysis of iron ores in which the iron was reduced in hydrochloric acid solution with stannous chloride, the excess of the latter being removed with mercuric chloride, because some of the present methods for titrating the iron after such a reduction have certain undesirable features. If permanganate is used as the oxidizing agent, the concentration of hydrochloric acid must be small because of its reducing action. Manganese sulfate is added<sup>22</sup> but even with this precaution the end-point obtained is fleeting, and some experience with the method is required for accurate results. This end-point has been determined electrometrically.<sup>23</sup> If the titration is made with dichromate, potassium ferricyanide may be used as an external indicator, an inconvenient process, or diphenylamine as an internal indicator,<sup>24</sup> the change in color being from a green to a deep blue shade. Many persons find it difficult to obtain a sharp color change in this latter case. The determination of the end-point electrometrically is very satisfactory.<sup>25</sup>

### Experimental

A standard iron solution was made by dissolving electrolytic iron (99.97% Fe) in hydrochloric acid. The ferrous chloride was largely oxidized by the addition of potassium chlorate. To 20 cc. of this solution, containing 0.3032 g. of iron, 5 cc. of hydrochloric acid, sp. gr. 1.18, was added and the reduction carried out with stannous chloride in the usual

<sup>21</sup> This Dissertation, pages 31 and 32.

<sup>22</sup> Barnebey, *J. A. C. S.*, **36**, 1429 (1914).

<sup>23</sup> Erich Müller, "Elektrometrische Massanalyse," Th. Steinkopff, Dresden, 1926, pp. 152-153; Müller and Möllering, *Z. anorg. allgem. Chem.*, **141**, 111 (1924).

<sup>24</sup> Knop, *J. A. C. S.*, **46**, 263 (1924); Mehlig, *J. Chem. Education*, **3**, 824 (1926).

<sup>25</sup> Hildebrand, *J. A. C. S.*, **35**, 847 (1913); Kolthoff, *Chem. Weekblad*, **16**, 450 (1919); Hostetter and Roberts, *J. A. C. S.*, **41**, 1337 (1919); Eppley and Vosburgh, *ibid.*, **44**, 2148 (1922).

way. The solution was cooled, diluted to 150 cc., 10 cc. of saturated mercuric chloride and the indicated volume of hydrochloric acid added, and the solution titrated with ceric sulfate which had been standardized against sodium oxalate.

TABLE VII

| RESULTS OBTAINED ELECTROMETRICALLY                 |                  |                                                                                                                                                 |
|----------------------------------------------------|------------------|-------------------------------------------------------------------------------------------------------------------------------------------------|
| HCl, sp. gr., 1.18, added<br>before titration, cc. | Error,<br>mg. Fe | Remarks                                                                                                                                         |
| 0                                                  | -0.1             | Very slight HgCl ppt.                                                                                                                           |
| 0                                                  | - .4             | Heavy HgCl ppt.                                                                                                                                 |
| 15                                                 | - .2             | Very slight HgCl ppt.                                                                                                                           |
| 15                                                 | - .3             | Heavy HgCl ppt.                                                                                                                                 |
| 30                                                 | - .2             | Heavy HgCl ppt.                                                                                                                                 |
| 50                                                 | ?                | No permanent break in potential<br>at end-point. Solvent action of<br>HCl on HgCl and reducing ac-<br>tion of latter probably re-<br>sponsible. |

Experiments similar to those above, in which 35 mg. of arsenic as sodium arsenite, or 15 mg. of manganese as manganese sulfate, or both, was added to the iron solution before reduction with stannous chloride, showed that neither of these elements caused any interference. Such would not be the case with arsenic in some other methods.

Since diphenylamine has been used as internal indicator in the ferrous iron titration with dichromate and the present author has found that diphenylbenzidine gave similar results, it seemed probable that either of these indicators might be applicable in the ferrous iron-ceric sulfate titration. Such was found to be the case, and the color change at the end-point with this latter oxidizing agent was far superior in sharpness to that obtained in a dichromate titration. This might be expected because the ceric salt is a stronger oxidizing agent than dichromate and also because the change from a green chromic salt color to a deep purple is much more difficult to see than that from a colorless cerous solution to the same deep purple shade.

The standard iron solution was reduced as described above. To the 150 cc. of solution were added 15 cc. of phosphoric acid, sp. gr. 1.37 (prepared by diluting acid of sp. gr. 1.75 with an equal volume of water), the stated volumes of hydrochloric acid and 0.1% diphenylamine (d.p.a.) or diphenylbenzidine (d.p.b.), after which it was titrated with ceric sulfate which had been standardized against sodium oxalate.

In the last two experiments the volume of the solution was 400 cc. at the beginning of the titration. The data in Table VIII show that no blank correction is required for 0.8 cc. of either indicator, the amount used to obtain a sharp end-point, but that a correction is necessary with larger amounts



TABLE VIII  
RESULTS OBTAINED WITH A VISUAL END-POINT

| HCl, sp. gr.<br>1.18, cc. | Indicator, 0.1% | Error,<br>mg. Fe | Character of color change        |
|---------------------------|-----------------|------------------|----------------------------------|
| 0                         | 0.8 cc. d.p.b.  | -0.3             | Very sharp                       |
| 15                        | 0.8 cc. d.p.b.  | - .3             | Satisfactory                     |
| 30                        | 0.8 cc. d.p.b.  | - .3             | Satisfactory                     |
| 0                         | 0.8 cc. d.p.a.  | - .2             | Very sharp                       |
| 15                        | 0.8 cc. d.p.a.  | - .3             | Satisfactory                     |
| 30                        | 0.8 cc. d.p.a.  | - .3             | Satisfactory                     |
| 5                         | 1.6 cc. d.p.b.  | - .4             | Satisfactory                     |
| 5                         | 3.2 cc. d.p.b.  | - .4             | Not so sharp as preceding one    |
| 5                         | 1.6 cc. d.p.a.  | ± .0             | Sharp                            |
| 5                         | 3.2 cc. d.p.a.  | + .8             | Not so sharp                     |
| 0                         | 0.8 cc. d.p.a.  | ± .0             | Development of color much slower |
| 0                         | 0.8 cc. d.p.b.  | - .3             | Development of color much slower |

of diphenylamine. If the end-point in a titration is overstepped it is possible to add a slight excess of standard ferrous sulfate solution, and after a few moments titrate to the end-point with ceric sulfate. The change in color of the indicator in the reverse titration is much slower in the strong acid solution than is the development of the color with the first drop excess of ceric salt—too slow to use it in the determination of cerium.

The consistent error of 0.2–0.3 mg. iron for 0.3 g. present, or approximately one part in a thousand, appearing in Tables VII and VIII, might easily be caused by oxidation by the air. The addition of 1 g. of cerous sulfate to the ferrous solution caused no increase in this error, so that its catalytic action, if any, is very slight. This error was found to disappear when the titrations were made in an atmosphere of carbon dioxide. A weight buret was used here. Because of the constancy of this error, it is possible in the analysis of iron ores either to standardize the ceric sulfate solution against oxalate and multiply by 1.001 or to standardize the solution against an iron ore of known value or electrolytic iron, using the same experimental technique as employed in the unknown ore analyses.

Three Bureau of Standards iron ores were analyzed and a summary of the results obtained is given in Table IX. Four-tenths to six-tenths g. samples were treated with 5 cc. of water and 25 cc. of concd. hydrochloric acid, and the material kept just below the boiling point until all of the ore was decomposed. The insoluble residue was filtered off, decomposed with hydrofluoric and sulfuric acids, and the salts remaining were taken up with dilute hydrochloric acid and returned to the main filtrate. Ore No. 29 contained so much silica that after treatment with hydrofluoric and a drop of sulfuric acids, the material was evaporated to dryness, a small amount of sodium carbonate added and the mixture fused for 3–4 minutes. The fusion was dissolved in dilute hydrochloric acid and added to the main solution. After evaporation to 10–15 cc., the solutions were

heated to boiling, reduced with a slight excess of stannous chloride, cooled, diluted to 150 cc., 10 cc. of saturated mercuric chloride solution was added and the titration with ceric sulfate made electrometrically. For the indicator method, 15 cc. of phosphoric acid (sp. gr. 1.37) and 0.8 cc. of indicator were added before the titration. In these analyses as well as in the standardization of the ceric sulfate against electrolytic iron (99.97% Fe) no carbon dioxide was used.

TABLE IX  
SUMMARY OF ANALYSES OF IRON ORES

| Ore             | Electrometric | d.p.a. | Indicator | d.p.b. |
|-----------------|---------------|--------|-----------|--------|
| B. of S. No. 27 | 69.21         | ...    |           | 69.25  |
| 69.26% Fe       | 69.27         | ...    |           | 69.26  |
|                 | 69.28         | ...    |           | ...    |
|                 | 69.23         | ...    |           | ...    |
| B. of S. No. 26 | 58.57         | 58.54  |           | ...    |
| 58.62% Fe       | 58.54         | 58.57  |           | ...    |
| B. of S. No. 29 | 55.75         | 55.73  |           | ...    |
| 55.75% Fe       | 55.80         | 55.70  |           | ...    |

Diphenylamine was found to be a much more satisfactory indicator than diphenylbenzidine. When ceric sulfate was added to an iron ore solution containing the latter indicator, a rather heavy, white precipitate formed which dissolved slowly. This difficulty was not encountered with diphenylamine.

Analyses were made of B. of S. ore No. 27, following the directions for the stannous chloride method through the fuming of the siliceous residue with hydrofluoric and sulfuric acids and the returning of this material to the main filtrate. Four cc. of concd. sulfuric acid was added to the solution and it was evaporated to fumes of  $\text{SO}_3$  to remove all hydrochloric acid. Twenty-five cc. of water was added to the moist residue and the liquid heated a few moments until a clear solution was obtained. Pieces of pure aluminum were added and the solution was boiled for ten minutes after it had become colorless. The aluminum was removed, the solution diluted to 150 cc. and the titration with ceric sulfate made electrometrically. For the indicator method, 15 cc. of phosphoric acid (sp. gr. 1.37) and 0.8 cc. of 0.1% diphenylamine were added before the titration. With the electrometric end-point the percentage of iron found was 69.20% and with the indicator 69.24%, both of which agree very well with the B. of S. value of 69.26%.

### Summary

1. Standard ceric sulfate may be used to titrate the iron in iron ores after a stannous chloride reduction in hydrochloric acid or a reduction with aluminum or zinc in sulfuric acid solution.
2. Arsenious acid does not interfere in the method.

3. The end-point in the titration may be determined electrometrically or with diphenylamine as internal indicator.

4. Analyses of three Bureau of Standards ores show that this method of titrating the ferrous iron is a very accurate one.

5. Because of the constancy of the slight error due to oxidation of the ferrous iron by air during a titration, the ceric sulfate solution may be standardized against sodium oxalate and a very small correction factor applied, or against a standard iron ore or electrolytic iron of known purity, using the same experimental technique as employed in the analyses.

### III. THE TITRATION OF IODIDE

#### Introduction

The electrometric titration of iodide with various oxidizing agents, both in the absence and presence of bromide and chloride, has been studied by a number of investigators. Crotogino<sup>26</sup> first described the use of potassium permanganate for this purpose. Later work carried out by Hendrixson,<sup>27</sup> Kolthoff,<sup>28</sup> and Müller and Möllering<sup>23b</sup> gave very accurate results in a sulfuric acid solution. The presence of an equivalent amount of bromide or of a large amount of chloride did not decrease the accuracy. In the presence of hydrochloric acid the reaction proceeded according to the equation:



but the authors gave no data to show the degree of accuracy of this reaction. Lang,<sup>29</sup> and Willard and Fenwick<sup>30</sup> titrated iodide in the presence of cyanide with permanganate, the latter authors using the potentiometric method. The end-point was reached when the iodide was changed quantitatively into iodine cyanide



The reaction was rapid, the end-point break very large, and bromide in moderate concentration or chloride in any amount<sup>30</sup> did not interfere.

When bromate was used as the oxidizing agent for iodide, Kolthoff<sup>31</sup> obtained theoretical results in a solution containing hydrochloric acid, though the reaction in the region of the end-point was very slow and the presence of bromide in the ratio of I:Br = 1:5 introduced an error. Hendrixson,<sup>32</sup> on the other hand, obtained theoretical results in a sulfuric acid solution but reported a considerable error for the titration in a hydrochloric acid solution. Kolthoff's<sup>31</sup> work with dichromate indicated this to be an unsatisfactory oxidizing agent in sulfuric acid solution but somewhat more

<sup>26</sup> Crotogino, *Z. anorg. Chem.*, **24**, 224 (1900).

<sup>27</sup> Hendrixson, *J. A. C. S.*, **43**, 14 (1921).

<sup>28</sup> Kolthoff, *Rec. trav. chim.*, **40**, 522 (1921).

<sup>29</sup> Lang, *Z. anorg. allgem. Chem.*, **122**, 332 (1922); **142**, 229 (1924).

<sup>30</sup> Willard and Fenwick, *J. A. C. S.*, **45**, 623 (1923).

<sup>31</sup> Kolthoff, *Rec. trav. chim.*, **39**, 208 (1920).

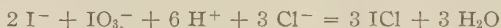
<sup>32</sup> Hendrixson, *J. A. C. S.*, **43**, 1309 (1921).



satisfactory in hydrochloric acid, though the accuracy in this latter medium was decreased by the presence of bromide. Hendrixson<sup>32</sup> found the direct titration with dichromate in a sulfuric acid solution possible, but the equilibrium in the region of the end-point was very slow.

Müller<sup>33</sup> titrated iodide electrometrically with ferricyanide in the presence of an excess of zinc sulfate, and obtained good results, though the reaction in the region of the end-point was slow. Willard and Fenwick<sup>30</sup> developed an accurate method unaffected by bromide or chloride by adding an excess of hypobromite to an alkaline iodide solution, and titrating the excess of oxidizing agent with arsenite.

According to Kolthoff<sup>31</sup> accurate results were obtained in the titration of iodide with iodate when the solution was acidified with either hydrochloric or sulfuric acids. The presence of bromide in moderate amount decreased the accuracy of the method. Hendrixson<sup>34</sup> found a sulfuric acid medium satisfactory but the reaction at the end-point was slower than when permanganate was the oxidizing agent. Müller and Junck<sup>35</sup> from work with this same titration recommended a sulfuric acid solution. In a hydrochloric acid solution they reported a break in potential at the completion of the reaction:



a statement which Kolthoff was unable to confirm. Müller<sup>23</sup> states that the action of periodate with iodide is very similar to that of iodate with iodide.

Previous work with ceric sulfate as a volumetric oxidizing agent suggested the importance of investigating potentiometrically the iodide-ceric salt reaction. Lange<sup>1</sup> stated that since ceric sulfate, even in the most dilute solutions, set free iodine from potassium iodide, it might be used as an oxidizing agent in volumetric analysis. Numerous investigators have made use of this reaction<sup>36</sup> as an iodimetric method for ceric cerium, their procedure being to treat the ceric salt with excess iodide in acid solution and to titrate the iodine liberated with thiosulfate. The direct titration of iodide with ceric sulfate, however, or the reverse reaction appears not to have been worked out. The following work describes the results obtained for these reactions in a hydrochloric or a sulfuric acid medium.

<sup>33</sup> Müller, *Z. anorg. allgem. Chem.*, **135**, 265 (1924).

<sup>34</sup> Hendrixson, *J. A. C. S.*, **43**, 858 (1921).

<sup>35</sup> Müller and Junck, *Z. Elektrochem.*, **31**, 200 (1925).

<sup>36</sup> Bunsen, *Ann. Chem.*, **86**, 285 (1853); Hartley, *J. Chem. Soc.*, **41**, 202 (1882); Browning, Hanford and Hall, *Z. anorg. Chem.*, **22**, 297 (1899); Browning, *Am. J. Sci.*, **158**, 451 (1899); Power and Shedden, *J. Soc. Chem. Ind.*, **19**, 636 (1900); Meyer and Koss, *Ber.*, **35**, 3740 (1902); Brauner, *Z. anorg. Chem.*, **34**, 207 (1903).

### Experimental

The 0.05 *N* potassium iodide, prepared from especially pure material, was standardized against potassium permanganate,<sup>37</sup> the normality of which had been determined with sodium oxalate. From two analyses the same factor, 0.05325 *N*, was obtained. The 0.1 *N* ceric sulfate was that prepared for earlier work and was 0.5 *M* in sulfuric acid. It was standardized against sodium oxalate. Measured portions of potassium iodide were taken, diluted with water and sulfuric acid to definite volumes and titrated electrometrically with 0.1 *N* ceric sulfate. The results are shown in Table X.

TABLE X  
TITRATION OF IODIDE WITH CERIC SULFATE IN SULFURIC ACID SOLUTION

| KI, 0.05 <i>M</i> ,<br>cc. | H <sub>2</sub> SO <sub>4</sub> (sp. gr. 1.25) at<br>beginning, cc. | Vol. at<br>beginning, cc. | KI,<br>normality |
|----------------------------|--------------------------------------------------------------------|---------------------------|------------------|
| 25                         | 0                                                                  | 100                       | 0.05324          |
| 25                         | 10                                                                 | 100                       | .05320           |
| 25                         | 50                                                                 | 100                       | .05324           |
| 25                         | 20                                                                 | 200                       | .05324           |
| 50                         | 0                                                                  | 100                       | .05320           |
| 50                         | 15                                                                 | 100                       | .05318           |
| 50                         | 15                                                                 | 200                       | .05320           |

The potential break at the end-point amounted to 175–200 mv. per 0.03 cc. of 0.1 *N* ceric sulfate. In the presence of bromide the break was decreased. With a ratio of I : Br = 5 : 1, it became 45 mv. per 0.03 cc. of 0.1 *N* solution. The iodide factor obtained above corresponds to the reaction



Thus, the titration of iodide in sulfuric acid solution with ceric sulfate or potassium permanganate, both of which have been standardized against the same primary standard, gives values which agree within less than 1 part in a thousand.

Measured portions of 0.1 *N* ceric sulfate were taken, diluted with water and sulfuric acid to 100 cc., and titrated electrometrically with 0.05 *M* potassium iodide. The results are shown in Table XI.

TABLE XI  
TITRATION OF CERIC SULFATE WITH IODIDE IN SULFURIC ACID SOLUTION

| Ce(SO <sub>4</sub> ) <sub>2</sub> ,<br>0.1 <i>N</i> , cc. | H <sub>2</sub> SO <sub>4</sub> (sp. gr. 1.83)<br>at beginning, cc. | KI, actual<br>vol., cc. | KI, theoretical<br>vol., cc. |
|-----------------------------------------------------------|--------------------------------------------------------------------|-------------------------|------------------------------|
| 25                                                        | 5                                                                  | 25.40                   | 25.36                        |
| 25                                                        | 10                                                                 | 25.38                   | 25.36                        |
| 15                                                        | 5                                                                  | 15.24                   | 15.22                        |
| 50                                                        | 5                                                                  | 50.75                   | 50.72                        |

<sup>37</sup> Müller and Möllering, *Z. anorg. Chem.*, **141**, 111 (1924), have shown that this titration is a very accurate one.

The potential break at the end-point amounted to 250–300 mv. per 0.03 cc. of 0.05 *M* iodide solution. The theoretical volumes were obtained by calculations from the data from two reverse titrations in which 25 cc. of potassium iodide required 24.66 and 24.64 cc. of ceric sulfate.

It was found possible to use this iodide titration after the bismuthate oxidation<sup>11</sup> of a cerous salt as a method for cerium. An approximately 0.05 *N* cerous sulfate solution was prepared from c. p. material. Fifty cc. portions of this solution, after oxidation with bismuthate and electrometric titration with ferrous sulfate which had been standardized electrometrically against standard ceric sulfate, were found from three analyses which agreed closely to contain 0.1745 g. of cerium. Table XII gives the corresponding data for analyses in which the ceric sulfate formed was titrated with potassium iodide which had been standardized electrometrically against a ceric sulfate solution of known strength.

TABLE XII  
DETERMINATION OF CERIUM

| $\text{Ce}_2(\text{SO}_4)_3$ , 0.05 <i>N</i> , cc. | Ce found               | Ce present |
|----------------------------------------------------|------------------------|------------|
| 25                                                 | 0.0873, 0.0874         | 0.0873     |
| 50                                                 | 0.1745, 0.1748, 0.1745 | 0.1745     |
| 100                                                | 0.3501, 0.3493, 0.3502 | 0.3490     |

### Titration in Hydrochloric Acid Solution

Measured portions of 0.05 *M* potassium iodide were taken, diluted with water to a definite volume, treated with hydrochloric acid according to the procedures described below and titrated electrometrically with 0.1 *N* ceric sulfate, forming iodine chloride. The potassium iodide is the same solution as in Table X. Therefore its factor should be  $2 \times 0.05321 \text{ } N$  or 0.1064 *N*, and was actually found to have this value by comparison with standard ceric sulfate. The results are given in Table XIII.

TABLE XIII  
TITRATION OF IODIDE WITH CERIC SULFATE IN HYDROCHLORIC ACID SOLUTION

| KI, 0.05 <i>M</i> ,<br>cc. | HCl (sp. gr. 1.18),<br>cc. | Vol. at beginning,<br>cc. | KI,<br>normality |
|----------------------------|----------------------------|---------------------------|------------------|
| 25                         | 55                         | 100                       | 0.1060           |
| 25                         | 45                         | 100                       | .1060            |
| 25                         | 35                         | 100                       | .1061            |
| 25                         | 25                         | 100                       | .1062            |
| 25                         | 45                         | 300                       | .1060            |
| 15                         | 45                         | 100                       | .1058            |
| 50                         | 45                         | 100                       | .1057            |

Nearly all of the ceric sulfate was added rapidly to the iodide solution from a pipet before the hydrochloric acid was poured in. An odor of iodine was noticeable in the experiments and this loss was undoubtedly the cause for the slightly low results. If the acid was added before the ceric sulfate,

the average factor obtained for the iodide was 0.1057–0.1058 *N*. When all but 0.2 cc. of the ceric sulfate, followed by the hydrochloric acid, was added to the iodide in a glass stoppered flask, the closed flask shaken thoroughly and its contents transferred to a beaker for the completion of the titration, the average factor from two closely agreeing titrations was 0.1061 *N*. Using a ratio of Br : I = 2 : 3, and 25 cc. of the iodide solution, the end-point break amounted to 30 mv. per 0.03 cc. of 0.1 *N* solution instead of 125–150 mv. for the same volume, the value obtained for the experiments in the table above. With 25 cc. of concd. hydrochloric acid per 100 cc., the reaction at the end-point was very slow; with less than this amount of acid, not practical.

Willard and Fenwick's<sup>30</sup> method of titrating iodide electrometrically in the presence of cyanide with permanganate, in which the iodide was changed quantitatively into iodine cyanide, was tested, using standard ceric sulfate instead of permanganate as the oxidizing agent. The reaction was found to be quantitative and the end-point reaction rapid.

A few experiments similar to those in Table XIII were made using standard potassium iodate instead of ceric sulfate. The factor of the iodide varied from 0.1056 *N* to 0.1061 *N* as the conditions were changed, indicating the same loss of iodine.

### Summary

1. Iodide may be determined very accurately in a sulfuric acid solution by electrometric titration to iodine with standard ceric sulfate. Moderate amounts of bromide may be present.

2. The titration of ceric sulfate with iodide in sulfuric acid solution goes smoothly and may be used in determining cerium after a bismuthate oxidation.

3. When iodide is titrated in a hydrochloric acid solution to iodine chloride with ceric sulfate, a small loss of iodine occurs during the oxidation and causes the results to be low—five parts or less in a thousand.



## IV. THE DETERMINATION OF ARSENIC

## V. THE DETERMINATION OF ANTIMONY

### Introduction

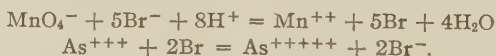
The action of cerium dioxide, either pure or impure, on arsenious acid in a hot sulfuric acid medium was investigated by Browning<sup>38</sup> who found that the oxide was only partially reduced. Job<sup>39</sup> in a paper on a method of induced oxidation of ceric carbonate stated that this compound did not oxidize potassium arsenite, but that in the presence of dextrose the latter was converted into arsenate. The direct titration of arsenious acid with a ceric salt, however, has not been tested, but such a reaction, if quantitative, would give another primary standard with which to compare such oxidizing solutions.

### Experimental

#### IV. THE DETERMINATION OF ARSENIC

A 0.1 *N* solution of sodium arsenite was prepared by dissolving pure arsenious oxide in sodium hydroxide, diluting and adding sulfuric acid until the solution was slightly acid, followed by 10 g. of potassium bicarbonate. The ceric sulfate solution was that prepared for earlier work and was 1 *M* in sulfuric acid. Preliminary experiments showed that the direct titration of arsenious acid with ceric sulfate in hydrochloric acid solution at room temperature was impossible. The reaction was too slow. If the reaction was carried out at 75–85°, the equilibrium was rapid and the end-point break amounted to 100–130 mv. per 0.03 cc. of 0.1 *N* oxidizing agent. At 70° or below, or with less than 15 cc. of concd. hydrochloric acid per 100 cc. of solution, the reaction was too slow to be satisfactory.

Lang<sup>40</sup> found that chloride, bromide and iodide ions catalyzed the action between arsenious and permanganic acids in sulfuric acid solution, stating that this titration with permanganate went smoothly if 0.5 cc. of 0.005 *N* potassium bromide was added to the boiling hot arsenious acid solution containing at least 25% sulfuric acid. He attributed the action of the bromide to the following reactions



Further work by this same author showed that the action of chloride alone as a catalyst was not satisfactory but that it served as a medium for the iodide catalysis at room temperature. Also, rather narrow experimental conditions had to be maintained when

<sup>38</sup> Browning, *Z. anorg. Chem.*, **22**, 297 (1899).

<sup>39</sup> Job, *Compt. rend.*, **134**, 1052 (1902).

<sup>40</sup> Lang, *Z. anorg. allgem. Chem.*, **152**, 197 (1926).

bromide was the catalyst. Iodine, iodide or iodate proved to be the most satisfactory. If the titration were carried out in a warm sulfuric acid solution, the presence of iodide would introduce a positive error, that of iodate, no error. In a hydrochloric acid solution iodide would cause a positive error and iodate a negative one, as the final form of the catalyst in either case is iodine monochloride. The amount of these catalysts required was so small, however, never more than 1 drop of 0.005 *N* solution, that any error caused by their presence was negligible. An explanation of the catalytic action of iodine in any of these three forms in the above reaction is given in Lang's paper.

A similar catalytic action with these materials in the arsenious acid-ceric salt titration might be expected. Potassium bromide was the first substance tested.

A 0.1 *N* sodium arsenite, prepared as directed above, was diluted with water and the stated amount of hydrochloric acid, sp. gr. 1.18, to a volume of 100 cc. This solution, to which potassium bromide was added, was titrated electrometrically at the indicated temperature with approximately 0.1 *N* ceric sulfate. The results are shown in Table XIV.

TABLE XIV  
CATALYTIC ACTION OF BROMIDE

| NaAsO <sub>2</sub> ,<br>0.1 <i>N</i> , cc. | HCl,<br>cc. | KBr,<br>g. | Temp.,<br>°C. | Ce(SO <sub>4</sub> ) <sub>2</sub> ,<br>0.1 <i>N</i> , cc. | Rate of the reaction                |
|--------------------------------------------|-------------|------------|---------------|-----------------------------------------------------------|-------------------------------------|
| 10                                         | 25          | 1.25       | 25            | 9.55                                                      | Too slow to be practical            |
| 10                                         | 25          | 2.50       | 25            | 9.55                                                      | More rapid—only fairly satisfactory |
| 10                                         | 25          | 5.00       | 25            | 9.56                                                      | Rapid—satisfactory                  |
| 10                                         | 35          | 2.50       | 25            | 9.56                                                      | Rapid—satisfactory                  |
| 10                                         | 35          | 5.00       | 25            | 9.55                                                      | Rapid—very satisfactory             |
| 10                                         | 50          | 1.25       | 25            | 9.52                                                      | Rapid—very satisfactory             |
| 10                                         | 50          | 0.00       | 25            | 9.57                                                      | Very slow—not practical             |
| 40                                         | 35          | 5.00       | 25            | 38.26                                                     | Very satisfactory                   |
| 10                                         | 25          | 1.25       | 70–75         | 9.50                                                      | Rapid                               |
| 10                                         | 25          | 0.50       | 70–75         | 9.52                                                      | Rapid                               |
| 10                                         | 25          | 0.25       | 70–75         | 9.56                                                      | Rapid                               |
| 10                                         | 25          | 0.12       | 70–75         | 9.58                                                      | Rapid                               |
| 10                                         | 25          | 0.00       | 70–75         | 9.58                                                      | Very slow—not practical             |
| 10                                         | 15          | 0.25       | 70–75         | 9.57                                                      | Rapid                               |
| 10                                         | 15          | .50        | 70–75         | 9.55                                                      | Rapid                               |
| 10                                         | 15          | 1.25       | 70–75         | 9.52                                                      | Rapid                               |
| 10                                         | 35          | 0.12       | 70–75         | 9.58                                                      | Rapid                               |
| 10                                         | 35          | .50        | 70–75         | 9.53                                                      | Rapid                               |
| 40                                         | 35          | .25        | 70–75         | 38.30                                                     | Rapid                               |
| 10                                         | 25          | 1.25       | 50–55         | 9.54                                                      | Quite rapid                         |
| 10                                         | 25          | 2.50       | 50–55         | 9.53                                                      | Rapid                               |
| 10                                         | 35          | 0.50       | 50–55         | 9.55                                                      | Rapid                               |

The break at the end-point was 60–80 mv. per 0.03 cc. of 0.1 *N* ceric sulfate when the titration was made at room temperature and 100–150 mv. for temperatures of 50–75°. The data show that the amount of bromide necessary for a rapid reaction decreases as the temperature or the hydrochloric acid content is increased, but it is always much greater than that required to catalyze the arsenite-permanganate reaction. The quantity of arsenite may be varied through wide limits, and results were identical whether the ceric sulfate was added slowly or the greater portion of it rapidly from a pipet.

Ten cc. of 0.1 *N* sodium arsenite, a different solution from that used in the experiments in Table XIV, was taken and diluted with water, the stated amount of hydrochloric acid (sp. gr. 1.18) and catalyst to a volume of 100 cc. The titration was made electrometrically with approximately 0.1 *N* ceric sulfate at room temperature. The results are shown in Table XV.

TABLE XV  
CATALYTIC ACTION OF IODINE OR IODINE CHLORIDE

| HCl,<br>cc.     | Catalyst,<br>cc.    | Ce(SO <sub>4</sub> ) <sub>2</sub> ,<br>0.1 <i>N</i> , cc. | Actual<br>blank, cc. | Theoretical<br>blank, cc. | Rate of the reaction                      |
|-----------------|---------------------|-----------------------------------------------------------|----------------------|---------------------------|-------------------------------------------|
| 35              | 5 g. KBr            | 10.18                                                     | ....                 | ....                      | A standardization                         |
|                 | KI, 0.0025 <i>M</i> |                                                           |                      |                           |                                           |
| 30              | 1                   | 10.25                                                     | +0.07                | +0.05                     | Rather slow                               |
| 30              | 2                   | 10.30                                                     | + .12                | + .10                     | Fairly rapid                              |
| 30              | 5                   | 10.47                                                     | + .29                | + .25                     | Rapid                                     |
| 30              | 7                   | 10.57                                                     | + .39                | + .35                     | Rapid                                     |
| 30              | 10                  | 10.72                                                     | + .54                | + .50                     | Very rapid                                |
| 30 <sup>a</sup> | 2                   | 10.31                                                     | + .13                | + .10                     | As rapid as preceding one                 |
| 40              | 5                   | 10.43                                                     | + .25                | + .25                     | No more rapid than with<br>30 cc. of acid |
|                 | ICl, 0.005 <i>M</i> |                                                           |                      |                           |                                           |
| 30              | 5                   | 10.17                                                     | — .01                | ....                      | Rapid                                     |
| 30              | 2.5                 | 10.17                                                     | — .01                | ....                      | Quite slow                                |
| 30              | 15                  | 10.16                                                     | — .02                | ....                      | Rapid                                     |
| 30              | 20                  | 10.17                                                     | — .01                | ....                      | Rapid                                     |
| 30 <sup>b</sup> | 5                   | 10.16                                                     | — .02                | ....                      | Rapid                                     |

<sup>a</sup> The temperature of the solution was 50–55° during the titration.

<sup>b</sup> Ten cc. of concd. sulfuric acid was added before the titration.

Titration were not made with potassium iodate as catalyst, because obviously iodine chloride, causing no blank correction, is the most convenient catalyst. The break at the end-point amounted to 150–250 mv. per 0.03 cc. 0.1 *N* ceric sulfate.

The iodine chloride solution was prepared by dissolving 0.279 g. of potassium iodide and 0.178 g. of potassium iodate in 250 cc. of water and adding at once 250 cc. of concd. hydrochloric acid.<sup>15</sup> The solution thus obtained was 0.005 *M* in iodine chloride. It was adjusted electrometrically by adding dilute potassium iodide or iodate.

In a titration in which either iodide or iodine chloride is used as catalyst the solution is somewhat yellow. When near the end-point, the color becomes deeper, due to the presence of considerable iodine, and during the addition of the last 0.5 cc. of ceric salt the color slowly bleaches as iodine chloride is formed. At the end-point the solution is still a pale yellow when the conditions are such that equilibrium is reached rapidly, or a slightly deeper yellow if less favorable conditions have been used. In the former case it is possible, after some experience, to determine the end-point visually, as the slightest excess of ceric salt causes the solution to become a deeper yellow again, but the method cannot be recommended as a sharp one.

A number of indicators were tested in the titration of arsenite with ceric sulfate in hydrochloric acid solution: methyl orange which is used in the arsenite-bromate reaction was not satisfactory, nor were indigo, diphenylamine or diphenylbenzidine. Methylene blue was the only indicator which appeared promising. A description of its use in the oxalate-ceric salt titration has been given<sup>41</sup> and the conditions for satisfactory results in the arsenite-ceric sulfate titration are the same: iodine chloride as catalyst, rapid reaction in the region of the end-point so that the yellow color bleaches quickly and addition of the indicator, 2 drops of 0.1% solution in water for each 100 cc. of solution, within 0.2–0.3 cc. of the end-point. In a series of experiments the amount of indicator was varied from 1 to 5 drops with excellent results and no blank correction in any case. The indicator works well also when the arsenic content of a solution is varied widely. The solution turns green when the indicator is added, and with each succeeding drop of ceric sulfate becomes more blue until a final drop or two of the oxidizing agent causes the whole liquid to turn a deep pink color, which in five to ten seconds changes to a permanent blue shade.

It has been shown previously<sup>42</sup> that the values of the factor obtained by standardizing ceric sulfate against (1) electrolytic iron, (2) sodium oxalate in hot solution, or (3) sodium oxalate at room temperature with iodine chloride as a catalyst were in very close agreement. At that time the conditions for the arsenite-ceric sulfate titration had also been worked out so that it was possible to include those standardizations. A weight buret was used for the ceric sulfate. The experimental conditions for the three methods mentioned above have been given in detail. For the arsenite-ceric salt titration, 0.25–0.30-g. samples of arsenious oxide of very accurately known purity were treated with 1 g. of sodium carbonate and 15 cc. of water and heated gently until solution was complete. The liquid was cooled, diluted with water to about 80 cc., 20 cc. of hydrochloric acid, sp. gr. 1.18, and 5 cc. of iodine chloride were added and the titration was made electrometrically with ceric sulfate. The results are shown in Table XVI.

TABLE XVI

| WEIGHT NORMALITY FACTOR OF CERIC SULFATE BY DIFFERENT METHODS |                                                                                |                                                                                                 |                                                              |
|---------------------------------------------------------------|--------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|--------------------------------------------------------------|
| Against (1) Electrolytic<br>Fe, 99.97%<br>Fe, <i>N</i>        | (2) Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub><br>in hot soln.,<br><i>N</i> | (3) Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub> at<br>room temp. ICl as<br>catalyst, <i>N</i> | (4) As <sub>2</sub> O <sub>3</sub> ,<br>99.985%,<br><i>N</i> |
| 0.09410                                                       | 0.09410                                                                        | 0.09406                                                                                         | 0.09381                                                      |
| .09414                                                        | .09416                                                                         | .09409                                                                                          | .09380                                                       |
| .09408                                                        | .09407                                                                         | .09409                                                                                          | .09379                                                       |
| .09408                                                        | .09406                                                                         | .09404                                                                                          | .09381                                                       |
| Average .09410                                                | .09410                                                                         | .09407                                                                                          | .09380                                                       |

<sup>41</sup> This Dissertation, pages 30 and 31.

<sup>42</sup> This Dissertation, page 33.



The normality factor from the standardization against arsenious oxide is about three parts in a thousand lower than that against electrolytic iron or oxalate, that is, more ceric salt has been required per equivalent weight of reducing agent in the former than in either of the latter cases. Two titrations were made in which the volumes of iodine chloride used were 10 and 15 cc., and the factors obtained were 0.09379 *N* and 0.09375 *N*. It would not be expected that the iodine chloride was responsible for the discrepancy as its use in the oxalate-ceric salt titration did not alter the results in the slightest degree. Since oxalate cannot be titrated with ceric sulfate in the presence of either phosphate or fluoride, because of the formation of insoluble salts, possibly double salts, it was thought that arsenate ion might behave in a similar way but the product is so soluble that only a slight error could be introduced. However, the addition of arsenate to either an oxalate solution or an arsenite solution at the beginning of a titration did not alter the volume of ceric salt required. There is as yet no explanation for this result, but from certain observations it seems possible that it may involve formation of double salts with cerium. In using this titration as a method for determining arsenic, accurate results may be obtained either by standardizing the ceric sulfate against arsenious oxide of known purity, or by multiplying the normality factor obtained from an oxalate titration by the correction factor 941/938, that is, 1.003.

## V. THE DETERMINATION OF ANTIMONY

In the determination of antimony by an electrometric titration of antimonous chloride with ceric salt, samples of the metal which had been analyzed carefully in connection with atomic weight work<sup>43</sup> were dissolved in hot, concd. sulfuric acid, the cool material diluted with water and concd. hydrochloric acid and solid sodium sulfite added, the excess of sulfur dioxide being removed by boiling. To be certain that a solution thus prepared contained all of the antimony in the trivalent form, a few titrations of such solutions were made electrometrically with potassium bromate, a method shown by Zintl and Wattenberg<sup>44</sup> to be accurate. The potassium bromate solution was made up directly by weight as its oxidizing strength had been accurately determined by comparing it against arsenious oxide of known purity. Zintl and Wattenberg call attention to the fact that it is necessary to make the titration quickly when working with a hot antimonous chloride solution because of oxidation by the air. To eliminate this error, carbon dioxide was used, and the greater part of the ceric sulfate added rapidly from a calibrated pipet and the last few cc. from a 10cc. buret.

<sup>43</sup> Willard and McAlpine, *J. A. C. S.*, **43**, 797 (1921).

<sup>44</sup> Zintl and Wattenberg, *Ber.*, **56**, 472 (1923).

From 0.35–0.45 g. of antimony (99.985%) was dissolved in 5 cc. of hot sulfuric acid, sp. gr. 1.83. To this, when cool, 20 cc. of water, 25 cc. of hydrochloric acid, sp. gr. 1.18, and 1 g. of sodium sulfite were added. The liquid was left on a low temperature hot-plate for ten minutes, then boiled for the stated time, the evaporated liquid being replaced at intervals by 1:1 hydrochloric acid, then diluted to 100 cc. and titrated electrometrically at 70–80° with 0.1083 *N* potassium bromate. The results are shown in Table XVII.

TABLE XVII  
TITRATION OF ANTIMONOUS CHLORIDE WITH POTASSIUM BROMATE

| Time and conditions of boiling to remove excess sulfite   | Factor obtained for<br>KBrO <sub>3</sub> soln., <i>N</i> |
|-----------------------------------------------------------|----------------------------------------------------------|
| 5 minutes while CO <sub>2</sub> bubbled through solution  | 0.1081                                                   |
| 10 minutes while CO <sub>2</sub> bubbled through solution | .1083                                                    |
| 20 minutes while CO <sub>2</sub> bubbled through solution | .1084                                                    |
| 30 minutes while CO <sub>2</sub> bubbled through solution | .1084                                                    |
| 5 minutes no CO <sub>2</sub>                              | .1075                                                    |
| 10 minutes no CO <sub>2</sub>                             | .1082                                                    |
| 20 minutes no CO <sub>2</sub>                             | .1082                                                    |
| 30 minutes no CO <sub>2</sub>                             | .1082                                                    |

Thus it is seen that theoretical results are obtained by boiling the solution for ten to thirty minutes in a stream of carbon dioxide, and the error is very small if carbon dioxide is not used.

Antimonous chloride solutions, similarly prepared, were cooled to room temperature, iodine monochloride added and titration made electrometrically with ceric sulfate. This titration at room temperature without a catalyst is too slow to be practical. Satisfactory results were not obtained at a higher temperature. Experiments with antimonous chloride solutions containing iodine chloride showed that methylene blue could be used as internal indicator in the titration with ceric salt.

### Procedure for Antimony

From 0.35–0.45 g. of antimony was dissolved in 5 cc. of hot sulfuric acid, sp. gr. 1.83. To this, when cool, the stated amounts of water and hydrochloric acid, sp. gr. 1.18, and 1 g. of sodium sulfite were added. The liquid was left on a low temperature hot-plate for ten minutes, then boiled for fifteen minutes while carbon dioxide was bubbled through the solution and the evaporated liquid was replaced at intervals by 1:1 hydrochloric acid, cooled and diluted to 100 cc.; 10 cc. of iodine chloride was added and titration made electrometrically with ceric sulfate, 0.1042 *N* against sodium oxalate. The results are shown in Table XVIII.

The break at the end-point varied considerably in magnitude, amounting in some cases to 40–50 mv. and in other instances, where the same experimental conditions had been maintained, to as much as 150–180 mv.

TABLE XVIII  
TITRATION OF ANTIMONOUS CHLORIDE WITH CERIC SULFATE

| H <sub>2</sub> O,<br>cc. | HCl,<br>cc. | Sb taken | Sb found |
|--------------------------|-------------|----------|----------|
| 20                       | 25          | 0.3617   | 0.3620   |
|                          |             | .3708    | .3708    |
|                          |             | .3804    | .3808    |
| 30                       | 15          | .3778    | .3773    |
|                          |             | .3362    | .3362    |
|                          |             | .3709    | .3710    |

per 0.03 cc. of 0.1 *N* ceric sulfate. The end-point was, however, never difficult to locate.

### Summary

1. Arsenious acid may be titrated accurately at 75–85° in hydrochloric acid solution with ceric sulfate, the end-point being determined electrometrically.

2. Potassium bromide may be used as a catalyst in this reaction and the titration made electrometrically either at room temperature or in hot solution. The amount of potassium bromide required for a rapid reaction decreases as the temperature or the hydrochloric acid content of the solution is increased.

3. Iodine has a greater catalytic effect, iodine monochloride being the most convenient form in which to use it, as its presence in a hydrochloric acid solution necessitates no blank correction. With this catalyst, the titration is made at room temperature, the end-point being determined either electrometrically or with methylene blue as an indicator.

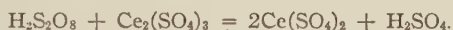
4. The normality factor of ceric sulfate obtained by comparison against arsenious oxide is about three parts in a thousand lower than that against oxalate. Therefore, in determining arsenic, the ceric sulfate should be standardized against arsenious oxide of known purity, or a correction be applied to the factor obtained from an oxalate titration.

5. Antimony may be accurately determined by electrometric titration of antimonous chloride with ceric sulfate at room temperature, iodine monochloride being present as catalyst, and the theoretical factor being used.

## VI. THE VOLUMETRIC DETERMINATION OF CERIUM

### Introduction

The persulfate<sup>45</sup> and bismuthate<sup>11</sup> oxidation methods for cerium have remained probably the most accurate as well as the most generally applicable of the many volumetric procedures proposed for this metal. The former method has been tested by a number of investigators,<sup>46</sup> all of whom found it accurate if the experimental conditions suggested by von Knorre were followed closely. The oxidation with persulfate was carried out in a solution containing just enough acid to prevent the precipitation of basic ceric salts, the reaction being



If too much acid was present, the oxidation of the cerous salt was incomplete. In the actual procedure, the persulfate was added in three or four portions, the solution boiled after each addition and finally boiled for about fifteen minutes to destroy excess persulfate. Such experimental technique is, obviously, tedious and inconvenient. The oxidation with persulfate has also been carried out in alkaline solution by Sterba-Boehm and Matula,<sup>47</sup> who dissolved the precipitate in potassium iodide and hydrochloric acid and titrated the iodine with thiosulfate, and by Autié,<sup>48</sup> who used nitric acid to dissolve the precipitate and hydrogen peroxide to determine the ceric salt. Either of these procedures involves a number of steps and consistent results were not obtained in the latter method. From this last paper one might be led to think that there were no accurate methods thus far for cerium, as the author's experimental data from a study of a number of volumetric oxidation methods leave much to be desired. Such, however, is not the case. His statement that the reaction of ceric ion with ferrous sulfate is somewhat reversible and that any method based upon this titration is consequently inaccurate, is absurd if one considers the oxidation-reduction potentials of the two systems involved.

<sup>45</sup> Von Knorre, *Z. angew. Chem.*, **11**, 717 (1897); *Ber.*, **33**, 1924 (1900).

<sup>46</sup> (a) Hintz and Weber, *Z. anal. Chem.*, **37**, 103 (1898); (b) Power and Sheddon, *J. Soc. Chem. Ind.*, **19**, 636 (1900); (c) Marc, *Ber.*, **35**, 2370 (1902); (d) Furman, *J. A. C. S.*, **50**, 755 (1928).

<sup>47</sup> Sterba-Boehm and Matula, *Rec. trav. chim.*, **44**, 400 (1925).

<sup>48</sup> Autié, *Bull. soc. chim.*, **41**, 1535 (1927).



Hydrogen peroxide may be used in this particular titration, as he suggests, but certainly has no advantage over ferrous sulfate in accuracy or stability.

In studying the action of oxidizing agents on cerous salts, Barbieri<sup>49</sup> found that silver nitrate catalyzed in an acid solution the oxidation of cerous nitrate or sulfate with persulfate and used this fact for the purification of crude cerium salts. However, he did not test the possibilities of the method quantitatively. Since his publication investigators have continued to use the original von Knorre method.<sup>46d,47,48,50</sup> The following material describes the much simpler technique which is possible in the presence of silver ion as catalyst.

### Experimental

**Titration with Ferrous Sulfate.**—The approximately 0.05 *N* cerous sulfate was prepared from c. p. material and contained 50 cc. of sulfuric acid, sp. gr. 1.83, per liter. Four analyses of 25cc. portions of this solution, using a bismuthate oxidation followed by electrometric titration of the ceric sulfate with standard ferrous sulfate, gave 0.1858, 0.1863, 0.1861 and 0.1858 g. of cerium. Definite amounts of this solution were taken; water, sulfuric acid and silver nitrate (containing 2.5 g. of silver nitrate per liter) were added to a total volume of 200 cc., followed by solid ammonium persulfate. The liquid was boiled for ten minutes, cooled to room temperature and titrated electrometrically with 0.05 *N* ferrous sulfate which had been standardized against ceric sulfate of known strength. A silver chloride-platinum electrode system was used. The vessel containing the silver chloride electrode in 0.1 *N* potassium chloride was placed directly in the liquid to be titrated. The quantities of the various materials and the results are shown in Table XIX.

TABLE XIX

OXIDATION WITH PERSULFATE—SILVER NITRATE AS CATALYST—TITRATION WITH FERROUS SULFATE

| Acid, cc.                                                | (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ,<br>g. | AgNO <sub>3</sub> ,<br>cc. | Ce taken,<br>g. | Ce found,<br>g. |
|----------------------------------------------------------|-----------------------------------------------------------------------|----------------------------|-----------------|-----------------|
| 2.5 cc. of H <sub>2</sub> SO <sub>4</sub> , sp. gr. 1.83 | 1                                                                     | 5                          | 0.1860          | 0.1863          |
| 2.5 cc. of H <sub>2</sub> SO <sub>4</sub> , sp. gr. 1.83 | 0.5                                                                   | 5                          | .1860           | low             |
| 2.5 cc. of H <sub>2</sub> SO <sub>4</sub> , sp. gr. 1.83 | 1                                                                     | 5                          | .1116           | .1118           |
| 2.5 cc. of H <sub>2</sub> SO <sub>4</sub> , sp. gr. 1.83 | 3                                                                     | 5                          | .3720           | .3722           |
| 2.5 cc. of H <sub>2</sub> SO <sub>4</sub> , sp. gr. 1.83 | 2                                                                     | 5                          | .3720           | .3719           |
| 10 cc. of H <sub>2</sub> SO <sub>4</sub> , sp. gr. 1.83  | 2                                                                     | 10                         | .1860           | .1859           |
| 10 cc. of H <sub>2</sub> SO <sub>4</sub> , sp. gr. 1.83  | 4                                                                     | 10                         | .1860           | .1860           |
| 10 cc. of H <sub>2</sub> SO <sub>4</sub> , sp. gr. 1.83  | 5                                                                     | 5                          | .1860           | .1858           |
| 10 cc. of H <sub>2</sub> SO <sub>4</sub> , sp. gr. 1.83  | 5                                                                     | 2.5                        | .1860           | .1856           |
| 5 cc. of H <sub>2</sub> SO <sub>4</sub> , sp. gr. 1.83   | 2                                                                     | 2.5                        | .1860           | .1860           |
| 5 cc. of H <sub>2</sub> SO <sub>4</sub> , sp. gr. 1.83   | 4                                                                     | 2.5                        | .3720           | .3722           |
| 5 cc. of HNO <sub>3</sub> , sp. gr. 1.42                 | 2                                                                     | 2.5                        | .1860           | .1858           |
| 10 cc. of HNO <sub>3</sub> , sp. gr. 1.42                | 4                                                                     | 2.5                        | .1860           | .1849           |
| 5 cc. of HClO <sub>4</sub> (70–72%)                      | 2                                                                     | 2.5                        | .1860           | low             |

From the data in Table XIX it is seen that the correct procedure for determining cerium is to use a sulfate solution containing 2.5–10 cc. of sulfuric acid, sp. gr. 1.83, per 200 cc., or a nitrate solution with 5 cc. of nitric acid, sp. gr. 1.42, in the same volume, add to this 1–5 g. of solid ammonium persulfate, depending on the amount of acid pres-

<sup>49</sup> Barbieri, *Atti R. Accad. Lincei*, 25, I, 37 (1916).

ent, 2–5 cc. of silver nitrate (containing 2.5 g. of silver nitrate per liter), boil for ten minutes, cool to room temperature and titrate electrometrically with standard 0.05 *N* ferrous sulfate.

The silver nitrate caused no interference during the titration, the end-point reaction was rapid, never more than a few seconds being required for the voltage to become steady and the break in potential averaged 200–250 mv. per 0.03 cc. of 0.05 *N* ferrous sulfate. A variation in volume between 100 and 300 cc. during the oxidation did not alter the results. The remarkable effect ascribed by Lindeman and Hafstad<sup>50</sup> to the presence of a considerable quantity of magnesium sulfate in the solution at the time of a persulfate oxidation was not apparent when silver nitrate was present. The persulfate procedure with silver ion as catalyst is simple and rapid, and has a certain advantage over the bismuthate method in which not only is a filtration required but also a blank determination on the technical bismuthate usually available.<sup>51</sup> Experiments to test the effect of the presence of other rare earths were not made, as the persulfate method has been shown<sup>45,46a,b</sup> to be applicable in such cases.

**Titration with Potassium Iodide.**—Since ceric nitrate or sulfate may be accurately titrated electrometrically with potassium iodide,<sup>52</sup> such a titration should be possible after a persulfate oxidation if a blank correction is made for the reaction between the silver nitrate and the iodide. To test this point, 15cc. portions of a ceric sulfate solution were taken, treated with 2.5 cc. of sulfuric acid, sp. gr. 1.83, and water to a volume of 200 cc. The stated amounts of silver nitrate (containing 2.5 g. of silver nitrate per liter) were added and the solution was titrated electrometrically with an approximately 0.05 *N* potassium iodide solution which had been standardized against ceric sulfate of known strength. The results are shown in Table XX.

TABLE XX  
IODIDE TITRATION OF CERIC SULFATE—SILVER NITRATE PRESENT

| No. | AgNO <sub>3</sub> ,<br>cc. | NaCl,<br>cc. | KI,<br>0.05 <i>N</i> , cc. | Blank<br>actual | Blank<br>calcd. |
|-----|----------------------------|--------------|----------------------------|-----------------|-----------------|
| 1   | 0                          | 0            | 24.33–24.32                | 0.00            | 0.00            |
| 2   | 1                          | 0            | 24.61                      | .28             | .27             |
| 3   | 2                          | 0            | 24.89                      | .56             | .54             |
| 4   | 4                          | 0            | 25.43                      | 1.10            | 1.09            |
| 5   | 6                          | 0            | 25.96                      | 1.63            | 1.63            |
| 6   | 2                          | 2            | 24.89                      | 0.56            | ..              |
| 7   | 2                          | 5            | 24.88                      | .55             | ..              |

The sodium chloride solution added before the titration in the last two experiments was of the same normality as the silver nitrate solution. The results for these two experiments show that the silver chloride is converted quantitatively into silver iodide during the titration. The values for the calculated blanks were obtained by considering the actual blank in Experiment 5 as correct and taking the proper aliquot portions of this value for the other blanks. The very close agreement between the actual and calculated blanks shows that the correction to be applied is strictly proportional to the amount of silver nitrate in solution.

<sup>50</sup> Lindeman and Hafstad, *Z. anal. Chem.*, **70**, 433 (1927).

<sup>51</sup> Someya, *Z. anorg. Chem.*, **168**, 56 (1927), states that a filtration is unnecessary, but he used a very pure grade of bismuthate in his work. He found, however, that he had to wait three to five minutes at the equivalent point for equilibrium to be established.

<sup>52</sup> This Dissertation, page 44.

Twenty-five cc. portions of the cerous sulfate used in Table XIX were diluted with water and acid to 200 cc., the persulfate oxidation was carried out in the presence of a measured amount of silver nitrate and the ceric sulfate and silver nitrate were titrated electrometrically with the same 0.05 *N* potassium iodide used in the experiments in Table XX. The weight of cerium present was 0.1860 g. The results are shown in Table XXI.

TABLE XXI  
OXIDATION WITH PERSULFATE-SILVER NITRATE AS CATALYST. TITRATION WITH POTASSIUM IODIDE

| No. | H <sub>2</sub> SO <sub>4</sub> , sp. gr.<br>1.83, cc. | (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ,<br>g. | AgNO <sub>3</sub> ,<br>cc. | KI,<br>0.05 <i>N</i> , cc. | Blank,<br>actual, cc. | Ce,<br>g. |
|-----|-------------------------------------------------------|-----------------------------------------------------------------------|----------------------------|----------------------------|-----------------------|-----------|
| 1   | 2.5                                                   | 1                                                                     | 2                          | 23.23                      | 0.55                  | 0.1862    |
| 2   | 2.5                                                   | 1                                                                     | 4                          | 23.78                      | 1.10                  | .1862     |
| 3   | 2.5                                                   | 1                                                                     | 1                          | less than<br>21 cc.        | ...                   | ...       |
| 4   | 5 cc. HNO <sub>3</sub> ,<br>sp. gr. 1.42              | 2                                                                     | 2                          | 23.21                      | 0.55                  | .1860     |

The actual blank correction for the silver nitrate was obtained by considering the difference between the volumes in Experiments 1 and 2, or 0.55 cc. as the volume of potassium iodide required by 2 cc. of silver nitrate solution. The amounts of cerium found in the 25cc. portions of the cerous sulfate solution agree very closely with the results in Table XIX as well as with the bismuthate analyses. The break in potential amounted to 100–150 mv. per 0.03 cc. of 0.05 *N* potassium iodide.

**Titration with Sodium Nitrite.**—The possibility of using sodium nitrite as the reducing agent for ceric ion after a persulfate oxidation was investigated. Measured portions of a standard ceric sulfate solution were taken, diluted with water and acid to a volume of 200 cc. and titrated electrometrically with 0.1 *N* sodium nitrite, the greater portion being added from a pipet beneath the surface of the liquid, the remainder in a similar way from a 10cc. buret. The temperature of the solution was 40–45°. The results are shown in Table XXII.

TABLE XXII  
NITRITE TITRATION OF CERIC SULFATE

| Ce(SO <sub>4</sub> ) <sub>2</sub> ,<br>0.1 <i>N</i> , cc. | Acid, cc.                                               | NaNO <sub>2</sub> ,<br>0.1 <i>N</i> , cc. |
|-----------------------------------------------------------|---------------------------------------------------------|-------------------------------------------|
| 20                                                        | 5 cc. of H <sub>2</sub> SO <sub>4</sub> , sp. gr. 1.83  | 17.18                                     |
| 20                                                        | 10 cc. of H <sub>2</sub> SO <sub>4</sub> , sp. gr. 1.83 | 17.15                                     |
| 20                                                        | 20 cc. of H <sub>2</sub> SO <sub>4</sub> , sp. gr. 1.83 | 17.23                                     |
| 50                                                        | 5 cc. of H <sub>2</sub> SO <sub>4</sub> , sp. gr. 1.83  | 42.82                                     |
| 20                                                        | 5 cc. of HNO <sub>3</sub> , sp. gr. 1.42                | 17.12                                     |
| 20                                                        | 10 cc. of HNO <sub>3</sub> , sp. gr. 1.42               | 17.12                                     |
| 20                                                        | 15 cc. of HNO <sub>3</sub> , sp. gr. 1.42               | 17.12                                     |
| 50                                                        | 10 cc. of HNO <sub>3</sub> , sp. gr. 1.42               | 42.82                                     |
| 10                                                        | 10 cc. of HNO <sub>3</sub> , sp. gr. 1.42               | 8.56                                      |

The results were not quantitative in perchloric acid solution. The reaction in the region of the end-point was very slow in sulfuric acid solution and slightly more rapid in nitric acid solution. The break in potential averaged 50–100 mv. in the former and 150–200 mv. in the latter cases per 0.03 cc. of 0.1 *N* sodium nitrite. With a temperature of 60°, the reaction at the end-point was somewhat more rapid and the values were not altered.

Two procedures were used for standardizing the nitrite solution: that of Busvold<sup>53</sup> depending on the reduction of silver bromate by nitrite and the weighing of the silver bromide formed, and that of Lunge<sup>54</sup> based on the titration of standard permanganate with nitrite. Laird and Simpson<sup>55</sup> tested both of these methods and found the gravimetric procedure accurate. In the volumetric method their results were not so exact, but they state that with sufficient care accurate results could probably be obtained. A series of preliminary titrations of 0.1 *N* potassium permanganate with 0.1 *N* sodium nitrite in solutions containing 10 cc. of sulfuric acid, sp. gr. 1.83, per 200 cc. showed that closely checking duplicates could be obtained and that the volume of nitrite solution varied strictly with the amount of permanganate used, if the precaution of adding the nitrite beneath the surface of the liquid was observed.

An approximately 0.1 *N* sodium nitrite solution was prepared from material containing only 0.002% of chloride. (1) 0.8 g. of silver bromate was dissolved in 200 cc. of water in a 500cc. flask at 80–85°, 100 cc. of the nitrite solution added from a pipet, followed by 30cc. of sulfuric acid, sp. gr. 1.2, the liquid being shaken thoroughly at this time and at frequent intervals to coagulate the silver bromide. After standing for three to four hours on the edge of the hot-plate, the precipitate was filtered, washed thoroughly with hot water and dried to constant weight. The same results were obtained when the silver bromate was dissolved in 2 *N* acetic acid,<sup>53</sup> provided that acetic acid distilled from chromic acid was used. With the ordinary c. p. acetic acid, the results were high, probably due to the presence of formic acid. (2) Fifty cc. portions of 0.06901 *N* permanganate, standardized against sodium oxalate, were treated with 165 cc. of water and 10 cc. of sulfuric acid, sp. gr. 1.83. Twenty-five cc. of nitrite solution was added from a pipet beneath the surface of the liquid; the solution was then heated slowly while the remainder of the nitrite was added in a similar way from a 10cc. buret. The end-point was determined electrometrically and the final temperature was 50–55°. (3) Twenty-five cc. portions of 0.09488 *N* ceric sulfate, standardized against sodium oxalate, were treated with 170 cc. of water and 50 cc. of nitric acid, sp. gr. 1.42, and titrated electrometrically at 40–45° with sodium nitrite, using the technique described above. The results are shown in Table XXIII.

These data indicate that accurate results may be obtained in the titration of permanganate with a reducing agent, a procedure which has been much debated. The author intends to investigate the permanganate–nitrite reaction in greater detail.

<sup>53</sup> Busvold, *Chem.-Ztg.*, **38**, 28 (1914).

<sup>54</sup> Lunge, *Ber.*, **10**, 1073 (1877).

<sup>55</sup> Laird and Simpson, *J. A. C. S.*, **41**, 524 (1919).



TABLE XXIII

| STANDARDIZATION OF SODIUM NITRITE SOLUTION |                        |         |
|--------------------------------------------|------------------------|---------|
| Method of standardization                  | Normality factor       | Average |
| Gravimetric                                | 0.1064, 0.1061, 0.1062 | 0.1062  |
|                                            | .1063                  |         |
| Titration of standard permanganate         | .1064, .1064, .1064    | .1064   |
| Titration of standard ceric sulfate        | .1064, .1064           | .1064   |

An accurate procedure for nitrite, based upon the addition of the nitrite solution to excess of standard ceric sulfate, followed by titration of the excess of the oxidizing agent with standard ferrous sulfate or potassium iodide, is obvious from the above experimental work.

### Determination of Cerium

Twenty-five cc. portions of the cerous sulfate solution used in Table XIX were diluted with water and 5 cc. of nitric acid, sp. gr. 1.42, to 200 cc., and the persulfate oxidation in the presence of silver nitrate was carried out in the usual way. The ceric sulfate was titrated electrometrically at 40–45° with the sodium nitrite standardized above. Three analyses gave 0.1855, 0.1859, 0.1859 g. of cerium, a close agreement with the average value 0.1860 g. of cerium from bismuthate oxidations.

Attempts to titrate the ceric sulfate with oxalate in hot solution in the presence of silver nitrate after having boiled the liquid for ten minutes to remove excess persulfate were not very satisfactory. The equilibrium was reached very slowly in the region of the end-point and the volume of oxalate required was slightly larger with silver nitrate present, but not proportional to the amount of this latter material. If the ceric sulfate solution was cooled to room temperature, considerable hydrochloric acid and 5 cc. of 0.005 *N* iodine chloride added, the titration with oxalate seemed to proceed rapidly but no end-point break could be obtained.

A few experiments were made to test the quantitative possibilities of two methods suggested by Barbieri:<sup>49</sup> (1) titration of cerous salt in strong sulfuric acid solution with permanganate, and (2) a similar titration in a dilute acid solution containing phosphoric acid. A visual end-point was impossible in the first method, due to the color of the ceric salt, and very difficult to obtain with even fair accuracy in the second method. A potentiometric end-point was impossible in either case, the slight solubility of the ceric phosphate probably being the source of trouble in the second method.

### Summary

1. Cerium may be accurately determined in the presence of the other rare earths by oxidation with persulfate in the presence of silver nitrate as catalyst, followed by electrometric titration with standard ferrous sulfate, potassium iodide or sodium nitrite. Hydrogen peroxide offers no advan-

tages in accuracy or stability of solution. The procedure in this oxidation method is much simpler and more rapid than that required in the original von Knorre persulfate method.

2. With potassium iodide a blank correction must be subtracted from the volume used because of the action between the silver and iodide ions.

3. With sodium nitrite the reaction in the region of the end-point is quite slow. The sodium nitrite solution, if practically free from chloride, may be standardized gravimetrically by weighing the silver bromide formed from the action between silver bromate and nitrite in acid solution. An alternative method is the electrometric titration of standard potassium permanganate with the nitrite solution.

## VII. THE DETERMINATION OF VANADIUM IN THE PRESENCE OF CHROMIUM, TUNGSTEN AND IRON

### Introduction

The following material deals with the use of ceric sulfate as a volumetric oxidizing agent, and describes the titration of vanadyl salts alone and in the presence of iron, chromium and tungsten. Such a study seemed important as permanganate is not entirely satisfactory in this reaction. Kelley and Conant<sup>56</sup> and Hamner<sup>57</sup> have described the permanganate titration of vanadyl sulfate in the presence of iron and of chromium, a method which is satisfactory except that the accurate determination of the end-point is difficult due to the color, and Kolthoff and Tomiček<sup>58</sup> have determined the end-point electrometrically, their end-point break being extremely poor. Zintl and Zaimis<sup>59</sup> have reported that they could not obtain accurate results, using Kolthoff and Tomiček's method, and the author has had the same experience. Some chromium was always oxidized. The following work shows that excellent results may be obtained when vanadyl salt is titrated with ceric sulfate.

### Experimental

The vanadyl sulfate was prepared by reduction of very pure ammonium vanadate in sulfuric acid solution with sulfur dioxide, and removal of the excess by boiling. It was standardized by electrometric titration in hot sulfuric acid solution with standard potassium permanganate; identical values of 0.1227 g. V were obtained from duplicate analyses of 20cc. portions of the solution. The ceric sulfate was a part of a supply made for earlier work and was 0.5 *M* in sulfuric acid. It was standardized against sodium oxalate. Measured portions of vanadyl sulfate were taken, acid and water added to a total volume of 100 cc. The solution was heated to 70–75° and titrated electrometrically with ceric sulfate. The results are shown in Table XXIV.

<sup>56</sup> Kelley and Conant, *Ind. Eng. Chem.*, **8**, 719 (1916).

<sup>57</sup> Hamner, *Met. Chem. Eng.*, **17**, 206 (1917).

<sup>58</sup> Kolthoff and Tomiček, *Rec. trav. chim.*, **43**, 447 (1924).

<sup>59</sup> Zintl and Zaimis, *Z. angew. Chem.*, **40**, 1286 (1927).

TABLE XXIV

## TITRATION OF VANADYL SALT WITH CERIC SULFATE

| Acid per 100 cc. of solution,<br>cc.                 | V taken,<br>g. | V found,<br>g. | Character of end-point |
|------------------------------------------------------|----------------|----------------|------------------------|
| 0                                                    | 0.1227         | 0.1224         | Fairly rapid           |
| 5 cc. H <sub>2</sub> SO <sub>4</sub> , sp. gr. 1.83  | .1227          | .1223          | Fairly rapid           |
| 10 cc. H <sub>2</sub> SO <sub>4</sub> , sp. gr. 1.83 | .1227          | ?              | Too slow               |
| 5 cc. HNO <sub>3</sub> , sp. gr. 1.42                | .1227          | .1217          | Fairly rapid           |
| 5 cc. HClO <sub>4</sub> , (70-72%)                   | .1227          | .1224          | Fairly rapid           |
| 10 cc. HClO <sub>4</sub> , (70-72%)                  | .1227          | .1224          | Rapid                  |
| 5 cc. HCl, sp. gr. 1.18                              | .1227          | .1225          | Rapid                  |
| 10 cc. HCl, sp. gr. 1.18                             | .1227          | .1228          | Rapid                  |
| 20 cc. HCl, sp. gr. 1.18                             | .1227          | .1234          | Rapid                  |
| 5 cc. HCl, sp. gr. 1.18                              | .0613          | .0612          | Rapid                  |
| 5 cc. HCl, sp. gr. 1.18                              | .3067          | .3061          | Rapid                  |

Thus, the titration is quantitative in a sulfuric, perchloric, or hydrochloric acid solution, the reaction at the end-point being more rapid with either of the two latter acids. Correct results may be obtained at room temperature, but the reaction is entirely too slow to be practical. The end-point break averaged 125-200 mv. per 0.05 cc. of 0.1 *N* ceric sulfate. Curve I, figure II, is an example of a titration in hydrochloric acid solution.

The titration of ceric sulfate with vanadyl sulfate was impossible at room temperature. At 70-80° the reaction was rapid with 5-15 cc. sulfuric acid per 100 cc. of solution, though the break at the end-point decreased as the sulfuric acid content was increased. Ten to twenty cc. of perchloric or 5-15 cc. of nitric acid per 100 cc. of solution was very satisfactory and the break at the end-point under these conditions averaged 125-175 mv. per 0.05 cc. of 0.1 *N* vanadyl sulfate. Table XXV gives data of typical titrations, showing that this is a satisfactory method of determining cerium after it has been oxidized to ceric salt. The total volume was 100 cc.

TABLE XXV

## TITRATION OF CERIC SALT WITH VANADYL SULFATE

| Acid per 100 cc. of solution,<br>cc.                 | Ce taken,<br>g. | Ce found,<br>g. |
|------------------------------------------------------|-----------------|-----------------|
| 5 cc. H <sub>2</sub> SO <sub>4</sub> , sp. gr. 1.83  | 0.3333          | 0.3341          |
| 15 cc. H <sub>2</sub> SO <sub>4</sub> , sp. gr. 1.83 | .3333           | .3339           |
| 10 cc. HClO <sub>4</sub> , (70-72%)                  | .3333           | .3336           |
| 20 cc. HClO <sub>4</sub> , (70-72%)                  | .3333           | .3328           |
| 5 cc. HNO <sub>3</sub> , sp. gr. 1.42                | .3333           | .3336           |
| 15 cc. HNO <sub>3</sub> , sp. gr. 1.42               | .3333           | .3333           |
| 5 cc. HNO <sub>3</sub> , sp. gr. 1.42                | .6666           | .6671           |
| 5 cc. HNO <sub>3</sub> , sp. gr. 1.42                | .1333           | .1326           |

## Effect of the Presence of Chromium and Iron

Using measured volumes of vanadyl sulfate, chromic sulfate, ferric sulfate and acid, and titrating these solutions electrometrically at 70-75°



with 0.05 *N* ceric sulfate, experiments showed that the oxidation of 10–60 mg. of vanadium in the presence of as much as 100 mg. of chromium and 5 g. of iron was selective in a sulfuric acid medium. Quantitative results were not obtained when nitric, perchloric or hydrochloric acid was substituted for sulfuric acid, though a moderate amount of nitric acid along with the sulfuric acid was not harmful. Manganese caused no interference.

### Effect of the Presence of Tungsten

The only method at the present time for determining vanadium in the presence of chromium, iron and tungsten is one described by the author.<sup>60</sup> There it was shown that tungsten as sodium tungstate solution may be poured into an acid solution containing considerable iron without any precipitation of tungstic acid. The ferric salt holds the tungstic acid in solution. Such a solution remains clear on boiling if sufficient iron is present. In the following work in which the solutions containing tungstic acid were not boiled but simply heated to 70–75°, a ratio of iron to tungsten of 5:1 was satisfactory, such solutions remaining clear during the experiment but becoming cloudy on standing.

Experiments were made with solutions containing the amounts of materials indicated in Table XXVI. The tungsten was added as sodium tungstate, and the solutions were diluted to 300 cc. Titration was made electrometrically at 70–75° with 0.05 *N* ceric sulfate.

TABLE XXVI  
EFFECT OF THE PRESENCE OF TUNGSTIC ACID

| H <sub>2</sub> SO <sub>4</sub> , sp. gr. 1.83,<br>present, cc. | Cr,<br>mg. | Fe,<br>g. | W,<br>g. | V taken,<br>g. | V found,<br>g. |
|----------------------------------------------------------------|------------|-----------|----------|----------------|----------------|
| 10                                                             | 50         | 1         | 0.2      | 0.0311         | 0.0313         |
| 10                                                             | 50         | 2         | .4       | .0311          | .0312          |
| 10                                                             | 50         | 3         | .6       | .0311          | .0312          |
| 10                                                             | 100        | 2         | .4       | .0311          | .0315          |
| 20                                                             | 100        | 2         | .4       | .0311          | .0312          |
| 10 + 5 cc. H <sub>3</sub> PO <sub>4</sub> , sp. gr. 1.37       | 50         | 3         | .6       | .0311          | .0310          |

The end-point break varied from 55–90 mv. per 0.05 cc. of 0.05 *N* ceric sulfate in all but the last experiment, in which it amounted to 32 mv. for the same volume of oxidizing agent. Therefore, the use of phosphoric acid as a means of holding the tungstic acid in solution is not to be recommended, not only because it is unnecessary but also because it makes the end-point less distinct.

### Determination of Vanadium in Chrome-Vanadium Steels

After the steel was dissolved in sulfuric acid, and nitric acid added to oxidize the iron, it was found that further treatment with a suitable oxidiz-

<sup>60</sup> This Dissertation, page 12.

ing agent was required to remove all carbonaceous and reducing material from the solution. An excess of permanganate or of ceric salt, followed by boiling, was not satisfactory. Persulfate in the presence of silver nitrate gave better results. However, after the addition of excess ferrous sulfate to this solution, the voltage was found to gradually increase, and if a titration was made at this stage with ceric sulfate, the volume of solution required between the  $\text{Fe}^{++} \rightarrow \text{Fe}^{+++}$  and  $\text{VO}^{++} \rightarrow \text{VO}_3^-$  end-points was slightly greater than the theoretical value, an indication that there was still reducing material in the solution. If the solution previously oxidized with silver and persulfate and treated with excess ferrous sulfate was allowed to stand for 10 minutes, treated with a slight excess of dilute permanganate, and then a slight excess of ferrous sulfate, the results for vanadium were quantitative. Therefore, this double oxidizing treatment was always adopted. For a sharp change in potential at the first end-point, a cold solution of fairly high acid concentration was most satisfactory, and at the second end-point, a hot solution of lower acid concentration. Curve II, Figure II, was obtained by the titration of such a solution. Results for chrome-vanadium steels are given in Table XXVII. The recommended procedure is given below.

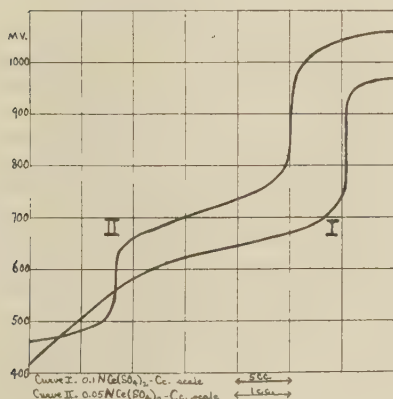


Fig. II.

Curve I. 20 cc. 0.1  $\text{N VO}_3^-$  titrated with 0.1  $\text{N Ce}(\text{SO}_4)_2$ ; 5 cc. conc.  $\text{HCl}$  in initial vol. 100 cc.

Curve II. Solution of a Cr-V steel containing excess  $\text{FeSO}_4$ . Titrated with 0.05  $\text{N Ce}(\text{SO}_4)_2$  to the  $\text{Fe}^{++} \rightarrow \text{Fe}^{+++}$  and  $\text{VO}^{++} \rightarrow \text{VO}_3^-$  end-points.

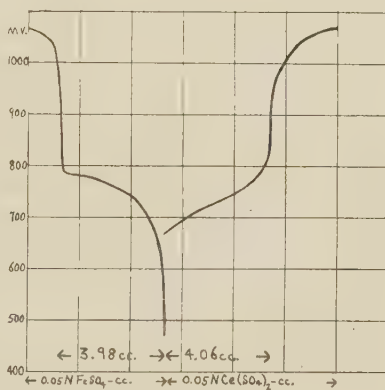


Fig. III.

Solution of a Cr-V steel containing excess  $\text{KMnO}_4$ . Titrated with standard 0.05  $\text{N FeSO}_4$  to the  $\text{MnO}_4^- \rightarrow \text{Mn}^{++}$  and  $\text{VO}_3^- \rightarrow \text{VO}^{++}$  end-points; then with standard 0.05  $\text{N Ce}(\text{SO}_4)_2$  to the  $\text{VO}^{++} \rightarrow \text{VO}_3^-$  end-point.

An alternative method for such a steel is to titrate to an end-point with ferrous sulfate, after a slight excess of permanganate has been added.

Then the titration with ceric sulfate will give the percent of vanadium. If the ferrous sulfate used in this direct titration is a standard solution, and if the  $\text{MnO}_4^- \rightarrow \text{Mn}^{++}$  end-point as well as the  $\text{VO}_3^- \rightarrow \text{VO}^{++}$  end-point is recorded, the volume of ferrous sulfate used between these two end-points should indicate directly the amount of vanadium in the solution, provided that no chromic salt was oxidized by the excess of permanganate. Calculations showed that the percent of vanadium obtained in this way never differed more than 0.005% from that obtained by the titration of vanadyl sulfate with ceric salt. Figure III shows such a titration curve.

Other experiments showed that ceric sulfate could be substituted for permanganate in the above treatment, and that in the subsequent titration with ferrous sulfate, reduction of ceric sulfate in the presence of vanadic acid was selective.

### Recommended Procedure for Chrome-Vanadium Steels

A sample of 4 or 5 g. is convenient when the percent of vanadium is low (0.15–0.25%). Place it in a 600cc. beaker, add 35–40 cc. of water and 10 cc.  $\text{H}_2\text{SO}_4$ , sp. gr. 1.83. After the steel has been completely decomposed, boil until a considerable quantity of salts separates out, in order to assist in decomposing carbides. Dilute with 20 cc. water and heat until the salts have dissolved. Add  $\text{HNO}_3$ , sp. gr. 1.42, drop by drop, to the hot liquid until the violent oxidation of  $\text{FeSO}_4$  is over (avoid more than 1 cc. excess). Boil the solution to destroy oxides of nitrogen. Dilute to 75–100 cc., add 2 cc.  $\text{AgNO}_3$  containing 2.5 g.  $\text{AgNO}_3$  per liter, 2 g.  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , and boil for 15 minutes. Cool to room temperature, add 40 cc.  $\text{H}_2\text{SO}_4$ , sp. gr. 1.5, and then dilute  $\text{FeSO}_4$  (0.05 *N* is convenient) until a 4–5 cc. excess is present as indicated by the voltage. After 10 minutes add a slight excess of dilute permanganate, cool the solution to 5–10°, and either add an excess of 0.05 *N* ferrous sulfate, or titrate to the  $\text{VO}_3^- \rightarrow \text{VO}^{++}$  end-point with ferrous sulfate, depending on the method being used. In the former case, the back titration with 0.05 *N*  $\text{Ce}(\text{SO}_4)_2$  to the  $\text{Fe}^{++} \rightarrow \text{Fe}^{+++}$  end-point is made in this cold solution. Then the solution is diluted to 300 cc., heated to 70–75°, and titrated with 0.05 *N*  $\text{Ce}(\text{SO}_4)_2$  to the  $\text{VO}^{++} \rightarrow \text{VO}_3^-$  end-point. In the latter case, after the direct titration with 0.05 *N*  $\text{FeSO}_4$  to the  $\text{VO}_3^- \rightarrow \text{VO}^{++}$  end-point, the solution is diluted to 300 cc., heated to 70–75°, and titrated with 0.05 *N*  $\text{Ce}(\text{SO}_4)_2$ .

### Determination of Vanadium in Chrome-Vanadium-Tungsten Steels

After the steel was dissolved in hydrochloric acid, the tungsten oxidized by nitro-hydrochloric acid, and the tungstic acid filtered off, sulfuric acid was added and the solution evaporated to fumes. This material was

diluted somewhat, and the tungstic acid added, after it had been converted into sodium tungstate solution either by dissolving in dilute sodium hydroxide, or by fusing with sodium carbonate in an open crucible and extracting with hot water. A clear solution was obtained. The use of persulfate or permanganate was unnecessary in this case after the nitro-hydrochloric treatment of the steel. Therefore, ferrous sulfate was added, either in excess, or to an end-point, depending upon the method used. Titration was then made with ceric sulfate, two end-points being obtained if excess of ferrous sulfate was used, otherwise one end-point. The conditions for sharp breaks were the same as for chrome-vanadium steels and the curves entirely similar to those already given. Results for a chrome-vanadium-tungsten steel are shown in Table XXVII. The recommended procedure follows.

### Recommended Procedure for Chrome-Vanadium-Tungsten Steels

A 1 g. sample is convenient for a steel containing 1% or more of V, and a 2 g. sample for a smaller percent of V. Add 10 cc. of water and 30 cc. HCl, sp. gr. 1.18, to the sample in a 400cc. beaker. Warm gently until the steel is completely decomposed and the W separates out as a black powder. To the boiling hot solution add 8 cc. HNO<sub>3</sub>, sp. gr. 1.42, at first cautiously, until the violent action is over. Boil, rotate the liquid frequently to expose a fresh surface of the W to the oxidizing agent, and evaporate to 20 cc. If there are any dark particles in the H<sub>2</sub>WO<sub>4</sub>, add 5 cc. HCl, 3 cc. HNO<sub>3</sub>, and boil down again. Dilute to 60–70 cc. with hot water, boil a few moments to dissolve any salts and let settle on the hot plate until the supernatant liquid is clear. Filter the H<sub>2</sub>WO<sub>4</sub>, using hot 2% HCl to transfer the precipitate and to wash it. Add 5 cc. H<sub>2</sub>SO<sub>4</sub>, sp. gr. 1.83, to the filtrate, and evaporate on a low temperature hot plate to fumes. Dilute to 70–80 cc. and heat until all salts have dissolved. Place a 150cc. beaker under the funnel containing the H<sub>2</sub>WO<sub>4</sub>, puncture the paper and wash through most of the H<sub>2</sub>WO<sub>4</sub> with water. Dissolve the remainder of the material on the filter with hot, 4% NaOH. Add 5–10 cc. more to the original beaker to dissolve any precipitate which adheres to the glass, using only about 15 cc. in all. Filter this liquid and pour the filtrate into the main filtrate from the H<sub>2</sub>WO<sub>4</sub> which has been diluted previously to 70–80 cc. A clear solution will result. Add 40 cc. H<sub>2</sub>SO<sub>4</sub>, sp. gr. 1.5, cool to 5–10°, and then add 0.1 N FeSO<sub>4</sub>, either in excess, or to the VO<sub>3</sub><sup>-</sup> → VO<sup>++</sup> end-point, depending on the method being used. From this point the procedure is the same as that given for chrome-vanadium steels.

### Summary of Analyses of Steels

In Table XXVII 4–5 g. samples of the chrome-vanadium steels were used, and 1–1.3 g. samples of the chrome-vanadium-tungsten steel.



TABLE XXVII  
VANADIUM IN ALLOY STEELS

| Steel                           | % Vanadium                                                                                                   |                                                                                                                                                       |
|---------------------------------|--------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                 | Excess $\text{FeSO}_4$<br>used—followed by<br>titration with $\text{Ce}(\text{SO}_4)_2$<br>to two end-points | $\text{FeSO}_4$<br>added to the $\text{VO}_3 \rightarrow$<br>$\text{VO}^{++}$ end-point—fol-<br>lowed by titration<br>with $\text{Ce}(\text{SO}_4)_2$ |
| Cr-V steel, No. I               | 0.230                                                                                                        | 0.234                                                                                                                                                 |
| 0.230% V-2.35% Cr               | .227                                                                                                         | .232                                                                                                                                                  |
|                                 | .232                                                                                                         |                                                                                                                                                       |
| B. of S. Cr-V steel, No. 30 (b) | .211                                                                                                         | .219                                                                                                                                                  |
| 0.215% V-1.03% Cr               | .212                                                                                                         | .216                                                                                                                                                  |
|                                 | .213                                                                                                         |                                                                                                                                                       |
| B. of S. Cr-V-W steel, No. 50   | .764                                                                                                         | .745                                                                                                                                                  |
| 0.756% V-3.61% Cr               | .751                                                                                                         |                                                                                                                                                       |

### Summary

1. Vanadyl ion may be determined volumetrically with ceric sulfate in hot sulfuric, hydrochloric, or perchloric acid solution. The titration of ceric salt with vanadyl sulfate proceeds quantitatively in hot sulfuric, nitric, or perchloric acid solution.

2. The oxidation of vanadyl ion by ceric sulfate in the presence of chromic salts, ferric salts, and tungstic acid, is selective in hot sulfuric acid solution. Also, the reduction of ceric ion by ferrous sulfate in the presence of vanadic acid is selective at room temperature.

3. Tungstic acid is kept in solution by dissolving it in sodium hydroxide and pouring it back into the original solution. In this soluble form it does not interfere.

4. Analyses of chrome-vanadium and chrome-vanadium-tungsten steels show that this method of determining vanadium is an accurate one.

## VIII. THE DETERMINATION OF CHROMIUM IN THE PRESENCE OF MANGANESE, IRON AND VANADIUM

### Introduction

The present volumetric methods for chromium depend upon its oxidation to the hexavalent form by an excess of some suitable reagent and its subsequent reduction, after removal of the excess oxidizing agent, by standard ferrous sulfate added either (1) directly to an end-point which may be determined either electrometrically, with diphenylamine or diphenylbenzidine<sup>61</sup> as internal indicator, or with ferricyanide as external indicator, or (2) in excess, the excess being determined by back titration with standard dichromate or permanganate. In the absence of oxidizing agents, such as ferric iron, excess iodide may be used as the reducing agent, the iodine liberated being titrated with thiosulfate. A method using arsenite<sup>62</sup> and another with excess arsenite, followed by back titration with bromate, have been described.<sup>63</sup> If persulfate in the presence of silver ions<sup>56</sup> is employed to oxidize the chromium, the excess is destroyed by boiling, and moderate amounts of manganese, converted into permanganate, are reduced to manganous salt by the addition of chloride ions and further boiling. If permanganate is the oxidizing agent, a filtration is always required. In certain cases oxidation is effected by peroxide in alkaline solution.<sup>64</sup> Thus it is seen that all of the methods in use require considerable time to remove the excess of oxidizing agent, and the presence of manganese always lengthens the time for an analysis.

A more rapid volumetric method for chromium, and one in which large amounts of manganese cause no interference or delay, is, therefore, highly desirable. The following material describes such a method in three different modifications: in one case the chromium is oxidized by a measured excess of standard ceric sulfate, the excess being titrated differentially in the

<sup>61</sup> The author has described the use of diphenylbenzidine as an indicator in the titration of chromic plus vanadic acids with ferrous sulfate. (This Dissertation, pages 14, 15 and 16). The results using this indicator are the same when chromic acid alone is titrated with ferrous sulfate.

<sup>62</sup> Zintl and Zaimis, *Z. angew. Chem.*, **40**, 1286 (1927); **41**, 543 (1928).

<sup>63</sup> Spitalsky, *Z. anorg. Chem.*, **69**, 179 (1910).

<sup>64</sup> The methods mentioned for which references have not been given are described in any of the standard reference texts on Analytical Chemistry or in special texts devoted to Steel Analysis.

presence of chromic acid with standard sodium nitrite or oxalate; in the second method the chromium is oxidized by excess ceric sulfate, nitrite added in slight excess to destroy the ceric salt, then urea to remove all nitrite, after which the chromic acid is titrated with standard ferrous sulfate; in the third method the chromium is oxidized by excess ceric sulfate, sodium azide added in excess to destroy the ceric salt and the chromic acid titrated with standard ferrous sulfate. In all three procedures iron may be present and also vanadium. With the latter element the sum of chromium and vanadium is determined, but it is possible to obtain the percentage of vanadium later with the same solution.

### Experimental

In the experimental work chromium was used in the form of a potassium chrome alum solution standardized by the persulfate method, vanadium as vanadyl sulfate and manganese as manganese sulfate. The ceric sulfate solution was that prepared for earlier work<sup>65</sup> and was 0.5 *M* in sulfuric acid. It was standardized against sodium oxalate.<sup>66</sup> The sodium nitrite,<sup>67</sup> ferrous sulfate<sup>68</sup> and vanadyl sulfate<sup>69</sup> solutions were standardized against ceric sulfate of known strength.

Preliminary experiments showed that the direct titration of chromic salt in hot solution with ceric sulfate was not possible although the oxidation is more rapid than with any other oxidizing agent. With an excess of ceric salt the oxidation of chromium was very rapid in hot solution. Before this reaction could be studied, a method for removing the excess of ceric salt had to be devised.

A number of reducing agents were tested for their differential possibilities by titrating them with 200 cc. of solution containing 20 cc. of 0.1 *N* ceric sulfate, 100 mg. of chromium as potassium dichromate, 0–40 mg. of vanadium as ammonium vanadate and varying amounts of acid. Using sodium nitrite the reduction of ceric sulfate was selective in the presence of 5–10 cc. of concd. nitric, sulfuric or perchloric acid. The temperature of the solution during titration was held between 50 and 60°. The reaction at the end-point was a little slow but satisfactory and the break in potential averaged 150–200 mv. per 0.05 cc. of 0.1 *N* sodium nitrite. Using sodium oxalate the reduction was selective with 2–5 cc. of concd. sulfuric acid or 5–20 cc. of concd. nitric or perchloric acid per 200 cc. The temperature during titration was 70–80°, the reaction at the end-point about as rapid as with nitrite and the break in potential from 100–150 mv. per 0.05

<sup>65</sup> This Dissertation, pages 25 and 26; also Furman, *J. A. C. S.*, **50**, 755 (1928).

<sup>66</sup> This Dissertation, pages 26, 27 and 28.

<sup>67</sup> This Dissertation, pages 56, 57 and 58.

<sup>68</sup> This Dissertation, pages 31 and 32; also Furman, *J. A. C. S.*, **50**, 755 (1928).

<sup>69</sup> Furman, *J. A. C. S.*, **50**, 1675 (1928); This Dissertation, pages 60 and 61.

cc. of 0.1 *N* oxalate. Experiments using either hydrogen peroxide or ferrous sulfate as the reducing agent were not successful.

### Oxidation of Chromium with Ceric Salt

**A. Use of Standard Ceric Sulfate and Titration of the Excess with Standard Sodium Nitrite.**—To measured portions of a standard solution of potassium chrome alum were added the indicated volumes of acid and standard ceric sulfate. The volume of the solution at the time of oxidation and the temperature maintained during the oxidation process are shown in Table XXVIII. After the oxidation the solution was diluted to 200 cc. and the excess ceric sulfate titrated electrometrically at 50–60° with standard sodium nitrite added from a buret with the tip beneath the surface of the liquid.

TABLE XXVIII

OXIDATION WITH EXCESS STANDARD CERIC SULFATE. TITRATION OF EXCESS WITH NITRITE

|                                  | Acid,<br>cc. | Vol. at time<br>of oxidation | Ce(SO <sub>4</sub> ) <sub>2</sub> ,<br>0.1 <i>N</i> , cc. | Temp. for<br>oxidation, °C. | Cr. taken,<br>g. | Cr found,<br>g. |
|----------------------------------|--------------|------------------------------|-----------------------------------------------------------|-----------------------------|------------------|-----------------|
|                                  | 5            | 100                          | 40                                                        | 65 for 5 min.               | 0.04557          | 0.04556         |
|                                  | 5            | 100                          | 30                                                        | 65 for 5 min.               | .04557           | .04525          |
| HNO <sub>3</sub>                 | 5            | 100                          | 30                                                        | 65 for 20 min.              | .04557           | .04556          |
| sp. gr.                          | 5            | 100                          | 40                                                        | 65 <sup>a</sup>             | .04557           | .04554          |
| 1.42                             | 5            | 200                          | 40                                                        | 65 for 5 min.               | .04557           | .04561          |
|                                  | 10           | 200                          | 40                                                        | 65 for 5 min.               | .04557           | .04561          |
|                                  | 5            | 150                          | 75                                                        | 65 for 5 min.               | .09114           | .09108          |
|                                  | 10           | 75                           | 40                                                        | 65 for 5 min.               | .04557           | .04355          |
| H <sub>2</sub> SO <sub>4</sub> , | 10           | 75                           | 40                                                        | 100 <sup>b</sup>            | .04557           | .04554          |
| sp. gr.                          | 10           | 75                           | 30                                                        | 100 <sup>b</sup>            | .04557           | .04487          |
| 1.5                              | 10           | 75                           | 30                                                        | 100 for 5 min.              | .04557           | .04562          |
|                                  | 20           | 100                          | 40                                                        | 100 <sup>b</sup>            | .04557           | .04552          |
| HClO <sub>4</sub> ,              | 5            | 100                          | 40                                                        | 100 <sup>b</sup>            | .04557           | .04562          |
| 70%                              | 5            | 100                          | 40                                                        | 65 <sup>a</sup>             | .04557           | .04556          |

<sup>a</sup> Solution heated to 65° and titrated at once.

<sup>b</sup> Solution heated to 100° and titrated at once.

Forty cc. of ceric sulfate for 45–46 mg. of chromium represents 12 cc. excess of oxidizing agent. The first four experiments show that the rate of oxidation of the chromium increases with the volume of ceric salt used. It is also seen that the oxidation proceeds more quickly in nitric or perchloric acid than in sulfuric acid solution. Variations in acid, volume of solution at time of oxidation and amount of chromium did not alter the accuracy of the method. Other experiments in which as much as 2 g. of iron or 24 mg. of vanadium or both were added were entirely satisfactory. In the presence of iron the reaction with nitrite was somewhat slower, although not more than ten to fifteen minutes was required for a titration and the break in potential was smaller, while in the presence of vanadium the ceric salt used for the oxidation gave accurately the vanadium plus



chromium content of the solution. In all later experiments the procedure of oxidizing the chromium with the ceric salt in a volume of 150 cc. by heating to 100° was adopted. If there was no nitric acid present, the solution was allowed to stand for three to five minutes before diluting it to 300 cc. and titrating with nitrite (this dilution gave the correct temperature for the nitrite titration). Such a procedure for chromium is obviously much more rapid than any in use at the present time.

### Stability of Nitrite Solution

The supply of 0.1 *N* sodium nitrite which was used over a period of five weeks remained constant in normality within less than one part in a thousand, even though the stock bottle was opened a number of times during this interval and no precautions were taken to exclude air. Thus nitrite has a decided advantage in this respect over a number of reducing agents.

**B. Use of Standard Ceric Sulfate and Titration of the Excess with Standard Sodium Oxalate.**—Solutions in which the oxidation of the chromium was carried out exactly as indicated in Table XXVIII were titrated electrometrically at 70–80° with standard sodium oxalate. These titrations were slightly more rapid than the nitrite reaction provided that iron was absent. Satisfactory results were obtained in the presence of as much as 1 g. of iron but with larger amounts the nitrite titration is to be preferred. Since sodium nitrite solution, however, is more stable than oxalate, it was used in the greater part of the later work.

**C. Use of Ceric Sulfate, Removal of the Excess with Nitrite Followed by Urea and Titration of Chromic Acid with Standard Ferrous Sulfate.**—Acid solutions of chromic salt similar to those described in Table XXVIII were prepared and the chromium oxidized in hot solution with an excess of ceric salt. After cooling to room temperature nitrite was added, from 5 to 15 cc. more than that required to destroy all ceric sulfate, followed at once by urea to remove excess nitrite. After the addition of 25 cc. of sulfuric acid, sp. gr. 1.5, the chromic acid was titrated electrometrically with standard ferrous sulfate. The results for chromium were always low, the error varying from 0.1–1.5 mg. according as 5 to 15 cc. excess of nitrite had been used. It seemed probable, therefore, that quantitative results could be obtained if the volume of nitrite was controlled more accurately. It was found that an excess of 0.25–0.50 cc. gave no trouble and the error with 1.0 cc. was very slight, provided always that any excess of nitrite was removed at once with urea. Results were identical whether the nitrite was added to the solution at room temperature or at 50–60°. In the method finally adopted the chromium was oxidized in hot solution in a volume of 150 cc., the solution diluted to 300 cc., 0.1 *N* sodium nitrite added in rapid drops until the potential indicated that an excess was pres-

ent, followed at once by 0.2–0.3 g. of urea. After adding sulfuric acid the solution was titrated with standard ferrous sulfate. Results obtained from a number of experiments are given later in Table XXIX.

### Effect of the Presence of Manganese. Nitrite Method

Preliminary experiments showed that a manganous salt is oxidized to a considerable extent in acid solution by ceric sulfate with the formation of permanganate, which changes to manganese dioxide if much manganese or nitric acid is present or if the solution is heated. It was also noticed that nitrite is very effective in dissolving manganese dioxide in acid solution. Solutions similar to those used in Table XXVIII, containing also varying amounts of manganese, were oxidized in a volume of 150 cc. with ceric salt. During the heating the permanganate color disappeared but a precipitate was not formed unless nitric acid was present, the manganese content high or the chromium content low. It appeared as if some of the manganese was oxidized first by the ceric salt to permanganate, which was effective in oxidizing chromium. The hot solution was diluted to 300 cc. and treated at once with excess nitrite followed by urea, as described in the preceding paragraph. After the addition of sulfuric acid, the chromic acid was titrated electrometrically with 0.1 *N* ferrous sulfate. Forty cc. of 0.1 *N* ceric sulfate, an approximately 10 cc. excess, was used for the oxidation. Results are given in Table XXIX.

In experiments in which a precipitate of manganese dioxide was formed, the nitrite had to be added slowly, drop by drop, especially if a nitric acid solution was used or much iron was present, to avoid an excess of nitrite at any time. The end-point was reached directly after the solution had cleared. If no  $\text{MnO}_2$  was present the nitrite could be added in much more rapid drops. The total time required for the determination of chromium by either method was seldom more than twenty minutes. Results were most satisfactory in perchloric and in sulfuric acid solutions, and only slightly less satisfactory in the sulfuric acid solutions containing nitric acid. With nitric acid alone quantitative results were obtained but the reduction of the  $\text{MnO}_2$  was quite slow. The experiments also show that the reducing action of the nitrite on the chromic acid becomes evident with a large excess of nitrite or with high acid concentration. It is seen that ferric salts are effective in preventing the formation of  $\text{MnO}_2$ . One extremely important point is that this procedure for chromium is accurate and simple, even in the presence of as much as 100 mg. of manganese.

Since the action between nitrite and  $\text{MnO}_2$  is quite rapid in many instances, the possibility of a direct titration with standard nitrite was investigated. Solutions prepared and oxidized as in Table XXIX were used. Representative results are shown in Table XXX:

Sulfuric or sulfuric and nitric acid solutions were most satisfactory,

TABLE XXIX

OXIDATION WITH CERIC SULFATE IN THE PRESENCE OF MANGANESE AND IRON. REMOVAL OF EXCESS OXIDIZING AGENT WITH NITRITE FOLLOWED BY UREA. TITRATION OF CHROMIC ACID WITH STANDARD FERROUS SULFATE

| Acid,<br>cc.<br>(H <sub>2</sub> SO <sub>4</sub> ,<br>sp. gr., 1.5) g.                                                             | Fe,<br>mg. | Mn,<br>mg. | V,<br>mg. | NaNO <sub>2</sub><br>excess,<br>0.1 N, cc. | Cr taken,<br>g. | Cr found,<br>g. | Remarks                            |
|-----------------------------------------------------------------------------------------------------------------------------------|------------|------------|-----------|--------------------------------------------|-----------------|-----------------|------------------------------------|
| 5                                                                                                                                 | 0          | 25         | 0         | 1.0                                        | 0.05342         | 0.05333         | Slight MnO <sub>2</sub> ppt.       |
| 5                                                                                                                                 | 0          | 25         | 0         | 2.0                                        | .05342          | .05312          | Slight MnO <sub>2</sub> ppt.       |
| 5                                                                                                                                 | 0          | 25         | 0         | 3.0                                        | .05342          | .05303          | Slight MnO <sub>2</sub> ppt.       |
| 2.5                                                                                                                               | 0          | 25         | 0         | 3.0                                        | .05342          | .05304          | Heavier MnO <sub>2</sub> ppt.      |
| 10                                                                                                                                | 0          | 10         | 0         | 1.0                                        | .05342          | .05308          | No MnO <sub>2</sub> ppt.           |
| 10                                                                                                                                | 0          | 10         | 0         | 0.25                                       | .05342          | .05335          | No MnO <sub>2</sub> ppt.           |
| 10                                                                                                                                | 0          | 100        | 0         | .25                                        | .05342          | .05335          | Heavy MnO <sub>2</sub> ppt.        |
| 10 <sup>a</sup>                                                                                                                   | 0          | 100        | 0         | .25                                        | .10684          | .10670          | Heavy MnO <sub>2</sub> ppt.        |
| 10 <sup>b</sup>                                                                                                                   | 0          | 100        | 0         | .25                                        | .02137          | .02132          | Heavy MnO <sub>2</sub> ppt.        |
| 10                                                                                                                                | 2          | 25         | 0         | 1.0                                        | .05342          | .05340          | No MnO <sub>2</sub> ppt.           |
| 5                                                                                                                                 | 2          | 25         | 0         | 1.0                                        | .05342          | .05338          | No MnO <sub>2</sub> ppt.           |
| 5 <sup>c,d</sup>                                                                                                                  | 2          | 25         | 24        | 1.0                                        | .05342          | .05333          | No MnO <sub>2</sub> ppt.           |
| (HNO <sub>3</sub> ,<br>sp. gr., 1.42)                                                                                             |            |            |           |                                            |                 |                 |                                    |
| 5                                                                                                                                 | 0          | 20         | 0         | 1.0                                        | .05342          | .05332          | Heavy MnO <sub>2</sub> ppt.        |
| 15                                                                                                                                | 0          | 10         | 0         | 1.0                                        | .05342          | .05330          | Heavy MnO <sub>2</sub> ppt.        |
| 5                                                                                                                                 | 0          | 50         | 0         | 1.0                                        | .05342          | .05338          | Heavy MnO <sub>2</sub> ppt.        |
| 5                                                                                                                                 | 2          | 25         | 0         | 1.0                                        | .05342          | .05349          | Slight MnO <sub>2</sub> ppt.       |
| 5 <sup>c,d</sup>                                                                                                                  | 2          | 25         | 24        | 1.0                                        | .05342          | .05368          | Slight MnO <sub>2</sub> ppt.       |
| (HClO <sub>4</sub> , 70%)                                                                                                         |            |            |           |                                            |                 |                 |                                    |
| 2.5                                                                                                                               | 0          | 25         | 0         | 1.0                                        | .05342          | .05341          | Slight MnO <sub>2</sub> ppt.       |
| 10                                                                                                                                | 0          | 25         | 0         | 0.25                                       | .05342          | .05343          | Slight MnO <sub>2</sub> ppt.       |
| 10                                                                                                                                | 2          | 25         | 0         | .25                                        | .05342          | .05340          | No MnO <sub>2</sub> ppt.           |
| H <sub>2</sub> SO <sub>4</sub> (sp. gr., 1.5) + HNO <sub>3</sub> (sp. gr., 1.42); 5 cc. of each acid in the following experiments |            |            |           |                                            |                 |                 |                                    |
| ..                                                                                                                                | 0          | 25         | 0         | 0.25                                       | .05342          | .05344          | Considerable MnO <sub>2</sub> ppt. |
| ..                                                                                                                                | 0          | 100        | 0         | .25                                        | .05342          | .05123          | Heavy MnO <sub>2</sub> ppt.        |
| ..                                                                                                                                | 0          | 75         | 0         | 1.0                                        | .05342          | .05335          | Heavy MnO <sub>2</sub> ppt.        |
| ..                                                                                                                                | 2          | 25         | 0         | 1.0                                        | .05342          | .05335          | No MnO <sub>2</sub> ppt.           |
| <sup>a</sup>                                                                                                                      | 2          | 25         | 0         | 1.0                                        | .10684          | .10653          | No MnO <sub>2</sub> ppt.           |
| <sup>b</sup>                                                                                                                      | 2          | 25         | 0         | 1.0                                        | .02137          | .02168          | Considerable MnO <sub>2</sub> ppt. |
| <sup>c,d</sup>                                                                                                                    | 2          | 25         | 24        | 1.0                                        | .05342          | .05322          | No MnO <sub>2</sub> ppt.           |

<sup>a</sup> 70 cc. of 0.1 N Ce(SO<sub>4</sub>)<sub>2</sub> used.

<sup>b</sup> 20 cc. of 0.1 N Ce(SO<sub>4</sub>)<sub>2</sub> used.

<sup>c</sup> 50 cc. of 0.1 Ce(SO<sub>4</sub>)<sub>2</sub> used.

<sup>d</sup> Solution cooled to 5–10° before titration with ferrous sulfate.

nitric acid solutions least so. Perchloric acid solutions were satisfactory in the absence of iron. With no MnO<sub>2</sub> precipitate the reaction between ceric salt and nitrite was rapid; otherwise, the precaution of adding the nitrite quite slowly to avoid any excess during the titration had to be taken. Even then a titration always required less than ten minutes if a sulfuric or sulfuric and nitric acid solution was used.

TABLE XXX

OXIDATION WITH STANDARD CERIC SULFATE IN THE PRESENCE OF MANGANESE AND IRON. DIRECT TITRATION WITH STANDARD NITRITE

| Acid<br>cc.<br>(H <sub>2</sub> SO <sub>4</sub> ,<br>sp. gr., 1.5)                                                                 | Fe,<br>g. | Mn,<br>mg. | V,<br>mg. | Cr taken,<br>g. | Cr found,<br>g. | Remarks                            |
|-----------------------------------------------------------------------------------------------------------------------------------|-----------|------------|-----------|-----------------|-----------------|------------------------------------|
| 5                                                                                                                                 | 0         | 10         | 0         | 0.05342         | 0.05347         | No MnO <sub>2</sub> ppt.           |
| 10                                                                                                                                | 0         | 75         | 0         | .05342          | .05364          | Considerable MnO <sub>2</sub> ppt. |
| 10                                                                                                                                | 0         | 100        | 0         | .05342          | .05282          | Considerable MnO <sub>2</sub> ppt. |
| 10                                                                                                                                | 2         | 20         | 0         | .05342          | .05364          | No MnO <sub>2</sub> ppt.           |
| 10                                                                                                                                | 1         | 75         | 0         | .05342          | .05367          | Heavy MnO <sub>2</sub> ppt.        |
| 10 <sup>a</sup>                                                                                                                   | 2         | 20         | 24        | .05342          | .05362          | No MnO <sub>2</sub> ppt.           |
| (HNO <sub>3</sub> ,<br>sp. gr., 1.42)                                                                                             |           |            |           |                 |                 |                                    |
| 5                                                                                                                                 | 0         | 20         | 0         | .05342          | .05358          | Considerable MnO <sub>2</sub> ppt. |
| 5                                                                                                                                 | 0         | 50         | 0         | .05342          | .05347          | Heavy MnO <sub>2</sub> ppt.        |
| 5                                                                                                                                 | 0         | 75         | 0         | .05342          | .05081          | Heavy MnO <sub>2</sub> ppt.        |
| 5                                                                                                                                 | 1         | 50         | 0         | .05342          | ?               | Too slow                           |
| 5                                                                                                                                 | 1         | 20         | 0         | .05342          | .05359          | Considerable MnO <sub>2</sub> ppt. |
| 5 <sup>a</sup>                                                                                                                    | 1         | 20         | 24        | .05342          | ?               | Very slow reaction                 |
| (HClO <sub>4</sub> , 70%)                                                                                                         |           |            |           |                 |                 |                                    |
| 2.5                                                                                                                               | 0         | 10         | 0         | .05342          | .05359          | No MnO <sub>2</sub> ppt.           |
| 10                                                                                                                                | 0         | 25         | 0         | .05342          | .05367          | Heavy MnO <sub>2</sub> ppt.        |
| 10                                                                                                                                | 1         | 20         | 0         | .05342          | .05364          | Slight MnO <sub>2</sub> ppt.       |
| H <sub>2</sub> SO <sub>4</sub> (sp. gr., 1.5) + HNO <sub>3</sub> (sp. gr., 1.42), 5 cc. of each acid in the following experiments |           |            |           |                 |                 |                                    |
| <sup>b</sup>                                                                                                                      | 0         | 20         | 0         | .10684          | .10699          | No MnO <sub>2</sub> ppt.           |
| <sup>c</sup>                                                                                                                      | 0         | 20         | 0         | .02137          | .02147          | Considerable MnO <sub>2</sub> ppt. |
| ..                                                                                                                                | 2         | 20         | 0         | .05342          | .05367          | No MnO <sub>2</sub> ppt.           |
| ..                                                                                                                                | 1         | 50         | 0         | .05342          | .05366          | Heavy MnO <sub>2</sub> ppt.        |
| <sup>a</sup>                                                                                                                      | 2         | 20         | 24        | .05342          | .05367          | No MnO <sub>2</sub> ppt.           |

<sup>a</sup> 50 cc. of 0.1 N Ce(SO<sub>4</sub>)<sub>2</sub> used.

<sup>b</sup> 70 cc. of 0.1 N Ce(SO<sub>4</sub>)<sub>2</sub> used.

<sup>c</sup> 20 cc. of 0.1 N Ce(SO<sub>4</sub>)<sub>2</sub> used.

### Effect of the Presence of Manganese. Oxalate Method

It was found that the direct titration of excess ceric sulfate with oxalate in the presence of MnO<sub>2</sub> precipitate after a chromium oxidation was slightly more rapid than the nitrite titration. In the oxalate method results accurate to a few hundredths of a milligram of chromium were always obtained in solutions containing 5–20 cc. of concd. nitric acid, 5–15 cc. of perchloric acid or 2 cc. of concd. sulfuric plus 5 cc. of concd. nitric acid per 200 cc., the titrations being made at 70–80°. In a sulfuric acid solution the reaction was quantitative but much slower, as was to be expected from earlier work.<sup>70</sup> The results were quantitative with as much as 40 mg. of manganese in the nitric acid solutions, or with 50 mg. of manganese in the perchloric or nitric plus sulfuric acid solutions. When the manganese precipitated out during the oxidation process, the oxalate was added in

<sup>70</sup> This Dissertation, pages 28 and 29.



rather slow drops. The results were satisfactory in the presence of 1 g. of iron, but with more iron the titration became very slow.

### Sodium Azide Method

Since hydrazoic acid may be determined by oxidation to nitrogen with excess ceric salt,<sup>6</sup> it seemed important to test the differential possibilities of this reagent for reducing ceric sulfate in the presence of chromic acid. In preliminary experiments 25 cc. of 0.1 *N* potassium dichromate was diluted with 10 cc. of sulfuric acid (sp. gr., 1.5) and water to a volume of 300 cc. Five to twenty cc. of 0.1 *M* sodium azide was added and the solution allowed to stand for thirty minutes before titration of the chromic acid with ferrous sulfate. A blank varying from -0.44 to -0.55 cc. was obtained, indicating slight reduction of the chromic acid by the hydrazoic acid. It was thought that some stronger reducing agent in the commercial sodium azide might be causing the trouble, though the blank varied only slightly when the azide content was changed from 5 to 20 cc. One portion of azide solution was purified by acidifying and distilling the hydrazoic acid into sodium hydroxide solution; another portion by acidifying, adding enough dichromate to destroy any stronger reducing agent present and to react with about 10% of the hydrazoic acid and distilling into sodium hydroxide. After adjustment to 0.1 *M*, 20cc. portions of these two solutions were tested for their action on dichromate, using the procedure described above. The blank in each case was -0.56 cc. Therefore nothing was accomplished by purifying the azide.

Experiments were then made involving the oxidation of a standard chromic salt solution with excess ceric sulfate, addition of excess azide and titration of the chromic acid electrometrically with standard ferrous sulfate. The oxidation procedure already described was used. After oxidation the solution was diluted to 300 cc., cooled to 35-40°, the amount of azide indicated in Table XXXI added (a solution of the commercial salt was used) and the solution allowed to stand for the given time. Twenty to 25 cc. of sulfuric acid (sp. gr., 1.5) was added and the chromic acid titrated. In the results given under the column "Cr found" in Table XXXI, a correction of +0.2 mg. of chromium has been added in every experiment, as an absolute error of this magnitude was always evident.

The hydrazoic acid acts more slowly on the manganese dioxide than either nitrite or oxalate. Six to eight minutes was always sufficient, however, to dissolve a heavy precipitate. Expts. 10 and 11 indicate that the azide may be added at a higher temperature without causing reduction of the chromic acid. In this warmer solution the effect of the hydrazoic acid may be unpleasant to some persons. If such experiments are conducted in a hood or the solution cooled to 35-40° before the azide is added, the odor of the acid is hardly noticeable. The tendency for the

TABLE XXXI

OXIDATION WITH CERIC SULFATE IN THE PRESENCE OF MANGANESE AND IRON. REMOVAL OF EXCESS OXIDIZING AGENT WITH SODIUM AZIDE. TITRATION OF CHROMIC ACID WITH STANDARD FERROUS SULFATE

| Acid<br>cc.<br>(H <sub>2</sub> SO <sub>4</sub> ,<br>sp. gr.,<br>1.5)                                                              | Fe,<br>g.        | Mn,<br>mg. | V,<br>mg. | NaN <sub>3</sub> ,<br>0.1 M,<br>cc. | Time<br>azide<br>acted, min. | Cr taken,<br>g. | Cr found,<br>g. | Remarks                            |
|-----------------------------------------------------------------------------------------------------------------------------------|------------------|------------|-----------|-------------------------------------|------------------------------|-----------------|-----------------|------------------------------------|
| 5                                                                                                                                 | 0                | 20         | 0         | 20                                  | 10                           | 0.05369         | 0.05367         | Considerable MnO <sub>2</sub> ppt. |
| 10                                                                                                                                | 0                | 25         | 0         | 20                                  | 10                           | .05369          | .05367          | No MnO <sub>2</sub> ppt.           |
| 20                                                                                                                                | 0                | 25         | 0         | 20                                  | 10                           | .05369          | .05364          | No MnO <sub>2</sub> ppt.           |
| 10                                                                                                                                | 0                | 25         | 0         | 20                                  | 5                            | .05369          | .05373          | No MnO <sub>2</sub> ppt.           |
| 10                                                                                                                                | 0                | 25         | 0         | 30                                  | 10                           | .05369          | .05364          | No MnO <sub>2</sub> ppt.           |
| 10                                                                                                                                | 0                | 25         | 0         | 50                                  | 10                           | .05369          | .05345          | No MnO <sub>2</sub> ppt.           |
| 10                                                                                                                                | 0                | 25         | 0         | 20                                  | 60                           | .05369          | .05364          | No MnO <sub>2</sub> ppt.           |
| 10                                                                                                                                | 0                | 25         | 0         | 20                                  | 12 hrs.                      | .05369          | .05292          | No MnO <sub>2</sub> ppt.           |
| 10                                                                                                                                | 0                | 25         | 0         | 30                                  | 60                           | .05369          | .05354          | No MnO <sub>2</sub> ppt.           |
| 10 <sup>a</sup>                                                                                                                   | 0                | 25         | 0         | 20                                  | 5                            | .05369          | .05364          | No MnO <sub>2</sub> ppt.           |
| 10 <sup>a</sup>                                                                                                                   | 0                | 25         | 0         | 20                                  | 10                           | .05369          | .05368          | No MnO <sub>2</sub> ppt.           |
| 10                                                                                                                                | 0                | 75         | 0         | 20                                  | 10                           | .05369          | .05370          | Considerable MnO <sub>2</sub> ppt. |
| 10                                                                                                                                | 0                | 100        | 0         | 20                                  | 10                           | .05369          | .05348          | Heavy MnO <sub>2</sub> ppt.        |
| 10                                                                                                                                | 2                | 25         | 0         | 20                                  | 10                           | .05369          | .05363          | No MnO <sub>2</sub> ppt.           |
| 10 <sup>b,e</sup>                                                                                                                 | 2                | 25         | 24        | 20                                  | 30                           | .05369          | .05360          | No MnO <sub>2</sub> ppt.           |
| 10 <sup>c</sup>                                                                                                                   | 0                | 25         | 0         | 20                                  | 10                           | .10738          | .10712          | No MnO <sub>2</sub> ppt.           |
| 10 <sup>d</sup>                                                                                                                   | 0                | 25         | 0         | 20                                  | 10                           | .02147          | .02152          | Considerable MnO <sub>2</sub> ppt. |
| (HNO <sub>3</sub> ,<br>sp. gr., 1.42)                                                                                             |                  |            |           |                                     |                              |                 |                 |                                    |
| 5                                                                                                                                 | 0                | 25         | 0         | 20                                  | 10                           | .05369          | .05373          | Considerable MnO <sub>2</sub> ppt. |
| 15                                                                                                                                | 0                | 25         | 0         | 20                                  | 10                           | .05369          | .05365          | Heavy MnO <sub>2</sub> ppt.        |
| 5                                                                                                                                 | 0                | 50         | 0         | 20                                  | 10                           | .05369          | .05365          | Heavy MnO <sub>2</sub> ppt.        |
| 5                                                                                                                                 | 2                | 25         | 0         | 20                                  | 10                           | .05369          | .05382          | Slight MnO <sub>2</sub> ppt.       |
| 10 <sup>b,e</sup>                                                                                                                 | 2                | 25         | 24        | 20                                  | 30                           | .05369          | .05373          | Very slight MnO <sub>2</sub> ppt.  |
| (HClO <sub>4</sub> , 70%)                                                                                                         |                  |            |           |                                     |                              |                 |                 |                                    |
| 5                                                                                                                                 | 0                | 25         | 0         | 20                                  | 10                           | .05369          | .05365          | Considerable MnO <sub>2</sub> ppt. |
| 10                                                                                                                                | 0                | 25         | 0         | 20                                  | 10                           | .05369          | .05364          | Slight MnO <sub>2</sub> ppt.       |
| 10                                                                                                                                | 2                | 25         | 0         | 20                                  | 10                           | .05369          | .05369          | No MnO <sub>2</sub> ppt.           |
| H <sub>2</sub> SO <sub>4</sub> (sp. gr., 1.5) + HNO <sub>3</sub> (sp. gr., 1.42), 5 cc. of each acid in the following experiments |                  |            |           |                                     |                              |                 |                 |                                    |
| ..                                                                                                                                | 0                | 50         | 0         | 20                                  | 10                           | .05369          | .05364          | Heavy MnO <sub>2</sub> ppt.        |
| ..                                                                                                                                | 0                | 75         | 0         | 20                                  | 15                           | .05369          | .05343          | Heavy MnO <sub>2</sub> ppt.        |
| ..                                                                                                                                | 2                | 25         | 0         | 20                                  | 10                           | .05369          | .05365          | No MnO <sub>2</sub> ppt.           |
| ..                                                                                                                                | 2 <sup>b,e</sup> | 25         | 24        | 20                                  | 30                           | .05369          | .05372          | No MnO <sub>2</sub> ppt.           |

<sup>a</sup> NaN<sub>3</sub> added to the solution at 60–65°.

<sup>b</sup> 45 cc. of 0.1 N Ce(SO<sub>4</sub>)<sub>2</sub> used.

<sup>c</sup> 70 cc. of 0.1 N Ce(SO<sub>4</sub>)<sub>2</sub> used.

<sup>d</sup> 20 cc. of 0.1 N Ce(SO<sub>4</sub>)<sub>2</sub> used.

<sup>e</sup> Solution cooled to 5–10° before titration with FeSO<sub>4</sub>.

results to be uniformly low by 0.2 mg. of chromium might indicate slight reduction of chromic acid, but the constancy of this error with variation in the amounts of chromium and azide used and in the time the azide acts is difficult to explain. The fact that an error of less than 1 mg. of chro-

mium is caused by leaving the hydrazoic acid in contact with the chromic acid for twelve hours shows that commercial sodium azide is an ideal substance for removing excess of ceric salt after a chromium oxidation. The method is rapid in the presence of large amounts of manganese.

A thermionic voltmeter, Type DP-2, purchased from the General Electric Company, was used for the titrations described in this paper. The instrument has infinite resistance and can therefore be connected directly to the platinum and silver chloride electrodes throughout a titration without danger of polarization. This makes unnecessary the use of a galvanometer or potentiometer and a continuous reading of the potential is obtained.

### Use of Indicator

After the excess of ceric sulfate has been reduced by a very slight excess of nitrite, and the latter destroyed by urea, the chromic acid may be titrated with ferrous sulfate, using about 0.3 cc. of 0.1% diphenylbenzidine or diphenylamine as indicator. Five to 10 cc. of phosphoric acid (85%) must be added and if the solution contains 2 cc. of concd. sulfuric acid in 200 cc. the end-point is sharp and cerous phosphate precipitates so slowly that the solution is hardly opalescent when the titration is finished. If 4 cc. of sulfuric acid is present, the end-point is less distinct but still fairly good. Cerous phosphate does not precipitate at all under these conditions. With more acid the end-point becomes very poor. If too much sulfuric acid is present, a suitable amount of sodium phosphate may be added.

The indicator method has no advantage over the electrometric, because in any case the latter is required to determine the amount of nitrite to be added.

When sodium azide is used to reduce the excess of ceric salt, the color of the indicator is so weakened that a satisfactory titration is impossible.

The application of the methods described above to the rapid determination of chromium in steel will be made the subject of a subsequent paper.

### Summary

1. A volumetric method for chromium, more rapid than any in use, has been developed. The chromium is oxidized with excess ceric salt, three possibilities in procedure being described: (a) oxidation with a measured excess of standard ceric sulfate, the excess being titrated differentially in the presence of chromic acid with standard sodium nitrite or oxalate; (b) oxidation with excess ceric sulfate, addition of nitrite in slight excess to destroy the ceric sulfate, followed by urea to remove all nitrite, after which the chromic acid is titrated with standard ferrous sulfate; (c) oxidation with excess ceric sulfate, the excess being removed with sodium

azide, and the chromic acid titrated with standard ferrous sulfate. The excess of nitrite must be small and the time of action short, while with azide a large excess acting for a considerable time has no reducing action on the chromium.

2. Iron does not interfere. If vanadium is present, the sum of the chromium and vanadium is determined.

3. The method is equally applicable and rapid in the presence of large amounts of manganese. Even though some of the latter may precipitate as manganese dioxide during the oxidation, it is readily dissolved by the reducing agent.

4. Diphenylbenzidine or diphenylamine may be used as indicator in method (b) but not in (c).



## IX. THE PREPARATION AND STABILITY OF SOLUTIONS

### Introduction

The method used by the author to purify U. S. P. cerous oxalate and to prepare a large supply of ceric sulfate has been described.<sup>71</sup> From subsequent work, especially from that dealing with the determination of vanadium and of chromium, it seemed important to investigate more thoroughly the grades of ceric oxide available in order to find the most convenient and inexpensive materials for use. Information concerning the stability of ceric sulfate solutions has also been obtained.

### Experimental

Solutions were prepared from four samples of ceric oxide kindly furnished by Dr. H. S. Miner of the Welsbach Company of Gloucester, New Jersey. The approximate amount of the oxide required for a liter of 0.1 *N* solution was taken, treated with sufficient sulfuric acid of the density indicated in Table XXXII to make the final solution 0.5 or 1 *M* in sulfuric

TABLE XXXII  
PREPARATION AND COST OF CERIC SULFATE SOLUTIONS

| Material                | Sp. gr. of $\text{H}_2\text{SO}_4$ used | $\text{H}_2\text{SO}_4$ in the $\text{Ce}(\text{SO}_4)_2$ soln., molar | G. of oxide per liter of 0.1 <i>N</i> soln. | Cost of oxide per liter of 0.1 <i>N</i> soln. based on price per 500 g. |
|-------------------------|-----------------------------------------|------------------------------------------------------------------------|---------------------------------------------|-------------------------------------------------------------------------|
| 1 High grade, anhydrous | 1.83                                    | 0.5                                                                    | 19.2                                        | \$0.17                                                                  |
|                         | 1.83                                    | 1.0                                                                    | 18.9                                        | .17                                                                     |
| 2 High grade, hydrated  | 1.5                                     | 0.5                                                                    | 22.5                                        | .15                                                                     |
|                         | 1.5                                     | 1.0                                                                    | 22.3                                        | .15                                                                     |
|                         | 1.3                                     | 0.5                                                                    | 24.0                                        | .16                                                                     |
| 3 Commercial, hydrated  | 1.5                                     | .5                                                                     | 46.9                                        | .05                                                                     |
|                         | 1.3                                     | .5                                                                     | 47.3                                        | .05                                                                     |
| 4 Commercial, anhydrous | 1.5                                     | .5                                                                     | 57.9                                        | .10                                                                     |

acid and the paste heated at the proper temperature until the conversion into ceric sulfate appeared complete. This material, when cool, was added to about 500 cc. of water, the liquid heated to 70–80° and filtered. The normality of the solution was determined with standard ferrous sulfate, and from this factor the weight of material required for a liter of 0.1 *N* solution was calculated as well as the cost of the ceric oxide for a liter of

<sup>71</sup> This Dissertation, pages 25 and 26.

such a solution, based on the price per 500 g. In large quantities the cost would be 20–30% less.

With Material 1, a temperature of 150–160° was maintained for a half hour to convert the oxide into sulfate. A small amount of the oxide was not attacked. Sample 2 was converted very rapidly by dilute sulfuric acid into ceric sulfate, a temperature of 130–135° being required with acid of sp. gr. 1.5 and 105–110° with acid of sp. gr. 1.3. The ceric sulfate in the former case dissolved in water to give an almost clear solution; in the latter case there was a small amount of unattacked oxide. Sample 3, when treated with acid of sp. gr. 1.5, was heated to 120–125°, and to 110° if treated with acid of sp. gr. 1.3. Sample 4, the commercial anhydrous material, was not satisfactory. The commercial hydrated oxide contained iron and phosphate and a considerable amount of precipitate settled out in solutions prepared from it. The solution decanted from this precipitate was found entirely satisfactory for chromium determinations<sup>72</sup> in which an excess of ceric sulfate was used as the oxidizing agent, the excess being destroyed by sodium azide or by sodium nitrite followed by urea<sup>72</sup> before the titration of the chromic acid with ferrous sulfate. Since the oxide for a liter of such a solution costs only four or five cents, depending upon whether the price per one-half kilo or per fifty kilos of oxide is used, the cost of the reagent for a single chromium determination is very small. There seems to be no reason why this commercial hydrated material cannot be used in all the methods described by the author except in the case of the titration of iodide where the ferric salt might cause trouble. Even when the high grade, hydrated oxide is used, the cost of the reagent is not excessive, being only ten to fifteen cents per liter, depending on the quantity of material purchased.

### Stability of Ceric Sulfate Solutions

Furman has given data over a period of twelve weeks on the stability of ceric sulfate solutions containing free sulfuric acid.<sup>9</sup> Table XXXIII

| TABLE XXXIII                                                 |           |        |         |         |
|--------------------------------------------------------------|-----------|--------|---------|---------|
| STABILITY OF CERIC SULFATE SOLUTIONS OVER AN EXTENDED PERIOD |           |        |         |         |
| Time, weeks                                                  | Normality |        |         |         |
|                                                              | I         | II     | III     | IV      |
| 0                                                            | 0.09493   | 0.1043 | 0.05012 | 0.09410 |
| 10                                                           | .09488    | .1042  | .05009  | ....    |
| 16                                                           | ....      | ...    | .04996  | ....    |
| 20                                                           | .09497    | ...    | ....    | ....    |
| 27                                                           | .09480    | ...    | ....    | ....    |
| 33                                                           | ....      | .1044  | ....    | .09400  |
| 40                                                           | ....      | .1042  | ....    | ....    |

contains data over a longer period obtained by the author on four different solutions.

<sup>72</sup> This Dissertation, pages 70, 71, 74 and 75.

Solutions I and III were 0.5 *M* in sulfuric acid, II and IV, 1.0 *M*. Twenty liters each of I and II and 2 liters of III were prepared, and the stock bottles were opened a number of times during the periods indicated. Only with Solution IV is the normality expressed in terms of weight normality. The values for this solution are the most accurate indication of the stability of ceric sulfate, for the portion tested after a 33-week interval had been standing during that time in a sealed flask in a well lighted room. These data indicate that ceric sulfate solutions are far more stable than permanganate solutions, the latter oxidizing agent being the only one which is of the same relative oxidizing power as ceric sulfate.

A number of experiments were made to test the stability of ceric sulfate solutions on boiling. In each case 25 cc. of 0.1 *N* solution was diluted with acid and water to a volume of 100 cc. This solution was boiled gently under a reflux condenser for the stated time, cooled to room temperature and titrated electrometrically with standard ferrous sulfate. The values for the normality after such treatment are given in Table XXXIV.

These results show that ceric sulfate solutions containing free sulfuric

TABLE XXXIV  
STABILITY OF CERIC SULFATE TOWARD HEAT

|                                        | Acid per<br>100 cc., cc.                             | Time of<br>boiling, hours | Normality<br>of $\text{Ce}(\text{SO}_4)_2$ |
|----------------------------------------|------------------------------------------------------|---------------------------|--------------------------------------------|
| $\text{H}_2\text{SO}_4$ , sp. gr., 1.5 | { 15                                                 | 0                         | 0.09322                                    |
|                                        | { 10                                                 | 2                         | .09322                                     |
|                                        | { 20                                                 | 2                         | .09322                                     |
|                                        | { 20                                                 | 5                         | .09322                                     |
| $\text{HNO}_3$ , sp. gr., 1.42         | { 10                                                 | 1                         | .09111                                     |
|                                        | { 5 + 10 cc. $\text{H}_2\text{SO}_4$ (sp. gr., 1.5)  | 1                         | .09328                                     |
|                                        | { 10 + 10 cc. $\text{H}_2\text{SO}_4$ (sp. gr., 1.5) | 1                         | .09288                                     |
| $\text{HClO}_4$ , 70%                  | { 5 + 10 cc. $\text{H}_2\text{SO}_4$ (sp. gr., 1.5)  | 1                         | .09322                                     |
|                                        | { 10 + 10 cc. $\text{H}_2\text{SO}_4$ (sp. gr., 1.5) | 1                         | .09310                                     |

acid, or sulfuric acid with moderate amounts of nitric or perchloric acid, are extremely stable toward heat. Such solutions, because of their strong oxidizing power, great stability, utility in a hydrochloric acid solution, ease of preparation and small cost, should find extensive use in analytical work.

### Summary

1. The types of ceric oxide available for the preparation of ceric sulfate have been investigated. A high grade, hydrated material supplied by the Welsbach Company meets the most exacting requirements, but the commercial, hydrated product is satisfactory in nearly all cases.

2. The cost of such solutions has been shown to be very small, that of

the oxide for a liter of 0.1 *N* solution from the high grade, hydrated material being ten to fifteen cents, and from the commercial, hydrated material four to five cents.

3. The normality of a ceric sulfate solution containing free sulfuric acid has been found to be practically constant over a period of forty weeks. Such a solution is not sensitive to light or air.

4. The normality of a ceric sulfate solution containing free sulfuric acid, or sulfuric acid with a little nitric or perchloric acid, is not changed by boiling the solution for an hour or longer, but the solution loses oxygen if a high concentration of either of the two latter acids is present.



## FURTHER APPLICATIONS

Two further uses for ceric sulfate as a volumetric oxidizing agent should be mentioned at this time. These particular reactions have been found to be quantitative but have not been studied in detail.

### The Determination of Thallium

The titration of thallous salt in hydrochloric acid solution with ceric sulfate was satisfactory as the following experiment will indicate. A weighed sample of thallous sulfate was taken, treated with 120 cc. of water and 8 cc. of hydrochloric acid, sp. gr. 1.18, and the material heated to boiling. The solution was titrated electrometrically at 80–85° with 0.1 *N* ceric sulfate. The potential remained low until the end-point was reached, indicating that no excess of ceric sulfate was present at any time. The amount of thallium in the sample of thallous sulfate was 0.3531 g., and the thallium found was 0.3533 g.

### The Titration of Ferrocyanide

Samples of an approximately 0.05 *N* potassium ferrocyanide solution were diluted with water and acid to 200 cc., and the solutions titrated electrometrically at room temperature with 0.1 *N* ceric sulfate. Results are shown in Table XXXV.

TABLE XXXV  
TITRATION OF FERROCYANIDE WITH CERIC SULFATE

| $K_4Fe(CN)_6$ ,<br>cc. | Acid, cc.                          | Normality factor<br>of ferrocyanide |
|------------------------|------------------------------------|-------------------------------------|
| 25                     | 10 cc. of $H_2SO_4$ , sp. gr. 1.83 | 0.05343                             |
| 50                     | 10 cc. of $H_2SO_4$ , sp. gr. 1.83 | 0.05343                             |
| 50                     | 10 cc. of $HCl$ , sp. gr. 1.18     | 0.05345                             |

The reaction was rapid in every case and the break in potential amounted to 200–300 mv. per 0.02 cc. of 0.1 *N* ceric sulfate.

In the preparation of this dissertation the author was assisted by the grant of a University of Michigan fellowship for the period 1926-1928.









